

Chemosensor Bibliography

Important Note: These are the articles that use the phrase "fluorescent chemosensor" in the title or abstract. There are many articles dealing with this subject that are not included in this list, simply because they do not include the phrase "fluorescent chemosensor" and therefore do not appear under this search. If the reader has citations they would like to have listed in this bibliography, please format them in the same way shown below and send the file to Administrator at admin@s4ms.com.

Intramolecular excimer formation and complexing behavior of tridentate pyridine podand having two naphthalene rings as a fluorescent chemosensor for zinc ion. Kawakami, Jun; Niiyama, Takuya; Ito, Shoei. Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University, Aomori, Japan. *Analytical Sciences* (2002), 18(7), 735-736.

Novel zinc fluorescent probe bearing dansyl and aminoquinoline groups. Jiang, Pengju; Chen, Lizhen; Lin, Jun; Liu, Qin; Ding, Jun; Gao, Xiang; Guo, Zijian. State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing, Peop. Rep. China. *Chemical Communications* (Cambridge, United Kingdom) (2002), (13), 1424-1425.

Abstract: A novel fluorescent chemosensor (L) demonstrates a remarkable selectivity and sensitivity for zinc(ii) ion as evidenced from the soln. characterisations and in vitro expts. using HeLa cell lines.

Fluorescent chemosensor for recognition of creatinine. Mei, Ming-Hua; Wu, Shi-Kang. Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, Peop. Rep. China. *Huaxue Xuebao* (2002), 60(5), 866-869.

Abstract: A fluorescent sensor for selective recognition of creatinine was synthesized. The formation of its complex with creatinine through hydrogen bonding interaction resulted in the improvement of fluorescence intensity of the sensor. The disturbance of several compds. such as urea and amino acid to the creatinine recognition of the sensor was tested. The result indicates that the artificial sensor obtained has specificity for the creatinine recognition.

New Fluorescent Chemosensors for Silver Ion. Kang, Jongmin; Choi, Miwhoa; Kwon, Ji Young; Lee, Eun Yeol; Yoon, Juyoung. Department of New Materials Chemistry, Silla University, Pusan, S. Korea. *Journal of Organic Chemistry* (2002), 67(12), 4384-4386.

Abstract: New fluorescent chemosensors, 1,8-bis(pyrazolylmethyl)anthracene and 9,10-bis(pyrazolylmethyl)anthracene, were synthesized. The 1,8-isomer showed selective fluorescent quenching effects with Ag(I) and Cu(II). However, the 9,10-isomer displayed a selective fluorescent quenching effect only with Ag(I). From the assocn. consts. obtained from fluorescent titrns. and by extn., rigid immobilization of the ligands, 1,8-isomer, plays a more important role in the binding with Ag(I) than the addnl. π -cation interaction offered by the 9,10-isomer.

A Highly Selective Fluorescent Chemosensor for Lead Ions. Chen, Chao-Tsen; Huang, Wan-Pei. Department of Chemistry, National Taiwan University, Taipei, Taiwan. *Journal of the American Chemical Society* (2002), 124(22), 6246-6247.

Abstract: A simple fluorescent chemosensor with ketoaminocoumarin as a signal-transducing unit exhibits a 40-fold fluorescence enhancement upon addn. of lead ion and yet is insensitive to most of univalent and divalent metal ions. The high affinity of chemosensor toward Pb²⁺ presumably results from the cooperative binding behaviors of two potential metal binding sites: the dicarbonyl and the 15-monoazacrown-5 ether.

Fluorescent chemosensors based upon macrocyclic polyamines containing aromatic sectors.

Bencini, Andrea; Bianchi, Antonio; Giorgi, Claudia; Valtancoli, Barbara. Department of Chemistry, University of Florence, Florence, Italy. *Journal of Inclusion Phenomena and Macrocyclic Chemistry* (2001), 41(1-4), 87-93.

Abstract: A review. The basicity and the coordination properties of several polyamine macrocycles contg. phenanthroline or dipyridine moieties as integral part of the cyclic framework are reported. The ligands behaves as fluorescent chemosensors for both H⁺ and metal ions. The use of such ligands in the prepn. of simple mol. machines, of chemosensors for metallohexacyanide anions, and of catalysts for photoinduced redox reaction is also described. The paper is a brief review of recent works performed by the authors.

Structural dependence of the selectivity of fluorescent chemosensors to Mg²⁺ from alkali earth metal ions.

Pei, Jian; Ding, Ai-Lin; Yu, Wang-Lin; Lai, Yee-Hing. Institute of Materials Research and Engineering, National University of Singapore, Singapore, Singapore. *Macromolecular Rapid Communications* (2002), 23(1), 21-25.

Abstract: Novel 2,2'-bipyridylene-contg. conjugated polymers were synthesized through the Wittig reaction. Some of these polymers show a highly selective affinity toward Mg²⁺ in a mixt. of alk. earth metal ions, which is different from the 2,2'-bipyridylene-contg. poly(phenylene vinylene) derivs. reported previously. This is the 1st case to demonstrate that some materials show a selectivity toward Mg²⁺. The structures of the polymers may play a crucial role for this selectivity.

Double naphthalene-tagged cyclodextrin-peptide capable of exhibiting guest-induced naphthalene excimer fluorescence.

Yana, Dewi; Shimizu, Tomoko; Hamasaki, Keita; Mihara, Hisakazu; Ueno, Akihiko. Department of Bioengineering, Graduate School of Bioscience and Biotechnology, Tokyo Institute of Technology, Yokohama, Japan. *Macromolecular Rapid Communications* (2002), 23(1), 11-15.

Abstract: A cyclodextrin-peptide hybrid (17NN β) bearing two naphthalene units in the peptide side chain has been designed and synthesized as a novel chemosensor mol. CD study of the compd. revealed that the peptide has α -helix structure with a helix content of 41%. The peptide revealed both monomer and excimer emission and the intensity of the excimer emission increased while that of the monomer emission decreased upon addn. of the guest compd. This behavior was obsd. for various guest mols., suggesting that the system can be used for detecting mols. in aq. soln.

Fluorescent signaling based on control of excited state dynamics. Biarylacetylene fluorescent chemosensors.

McFarland, Sherri A.; Finney, Nathaniel S. Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA, USA. *Journal of the American Chemical Society* (2002), 124(7), 1178-1179.

Abstract: We have previously reported that metal ion binding could restrict the excited state rotation of a biaryl chromophore, suppressing intersystem crossing and leading to increased emission. We have now applied the restriction of excited state dynamics to suppression of the other fundamental nonradiative decay pathway, internal conversion, in biarylacetylenes. This indicates that both nonradiative decay pathways are subject to conformational control, and that this signaling pathway should be generally accessible in simple flexible fluorophores.

Ab initio molecular orbital study of the complexing behavior of N-ethyl-1-naphthalenecarboxamide as fluorescent chemosensors for alkali and alkaline earth metal ions.

Kawakami, Jun; Miyamoto, Ryo; Fukushi, Atsuo; Shimozaki, Katsuyoshi; Ito, Shoei. Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University, Hirosaki, Aomori, Japan. *Journal of Photochemistry and Photobiology, A: Chemistry* (2002), 146(3), 163-168.

Abstract: N-ethyl-1-naphthalenecarboxamide (1NEa) was synthesized as a ref. compd. of the 1,n-bis(1-naphthalenecarboxamido)oxaalkanes (1NSN and 1NLN) having two naphthalene rings as fluorescent chemosensors for metal ions using intramol. excimer emission. However, large changes in the fluorescence

spectra of 1NEa having only one naphthalene ring as well as 1NSN and 1NLN were obsd. with the addn. of some metal ions. Therefore, the ab initio MO calcns. (Gaussian 98) using both the Hartree-Fock SCF and d. functional theory methods with 6-31G and 6-31+G(d) basis sets were carried out for 1NEa and its metal complexes to investigate the complexing behavior. The results of the MO calcns. suggest that 1NEa can form a complex with a metal ion by coordination with both the carbonyl oxygen of the amide group and π -electrons of the naphthalene ring.

General synthetic methods for the preparation of pinwheel receptors. Raker, Joseph; Glass, Timothy E. Department of Chemistry, The Pennsylvania State University, University Park, PA, USA. *Tetrahedron* (2001), 57(52), 10233-10240.

Abstract: The synthesis of bis-trityl diyenes, used as cooperative fluorescent chemosensors, is described. The most convenient sequence for the prepn. of the sensor framework was found to be intolerant of most functionality. Therefore, an unfunctionalized framework is constructed and recognition elements are selectively installed via electrophilic substitution on an electronically differentiated key intermediate. A divergent synthesis of a general class of chem. sensors emerges. This synthetic method is highlighted by its simplicity and modularity allowing for the introduction of various recognition elements and fluorophores.

Self-Assembling in Surfactant Aggregates: An Alternative Way to the Realization of Fluorescence Chemosensors for Cu(II) Ions. Berton, Matteo; Mancin, Fabrizio; Stocchero, Giulia; Tecilla, Paolo; Tonellato, Umberto. Department of Organic Chemistry and Centro CNR Meccanismi di Reazioni Organiche, University of Padova, Padua, Italy. *Langmuir* (2001), 17(24), 7521-7528.

Abstract: The self-assembling of the proper subunits of fluorescence chemosensors within surfactant aggregates in water allows the easy design, realization, and testing of new effective sensing systems. A proper ligand and a fluorescent dye, once transferred from bulk water into an inert surfactant aggregate, are kept in such a close proximity that communication between the binding site and the signaling unit effectively occurs, thus avoiding the need for a covalent connection between the sensor's two units. To further simplify the sensing system and get rid of the inert surfactant which somehow implies the diln. of the sensor's active components in the aggregate, the authors synthesized lipophilic ligands for Cu(II) based on dipeptides GlyLys and GlyGlu functionalized with n-alkyl chains of different lengths at the N-terminus. These ligands are sol. in water and can form homoaggregates in the absence and in the presence of Cu(II) ions. Lipophilic fluorophores, like 8-anilino-naphthalensulfonic acid or Rhodamine 6G, are effectively bound into the aggregate pseudophase, and the binding of Cu(II) ions to the dipeptide units causes a strong fluorescence quenching. The sensor system is very sensitive to Cu(II) (concns. in the submicromolar range are detected), is promptly reversible, and no interference is obsd. due to the presence of many metal ions. The sensitivity of the systems improves by decreasing the ligand concn. and (up to a point) the ligand's cmc.

A new fluorescent chemosensor for Cu²⁺ based on a dianthracene-derivative. Ostaszewski, R.; Klonkowski, A. M.; Kledzik, K. Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Pol. *Supramolecular Chemistry* (2000), 12(1), 131-134.

Abstract: A new class of photoinduced electron transfer (PET) chemosensors was tested for discrimination of Cu²⁺ and Ni²⁺ (or Zn²⁺) cations. The chemosensor consists of a metal-binding dioxodiamino unit linked to two light-emitting anthracene fragments. This type of supramols. when irradiated in methanol soln. (conc. 1.89.10⁻⁵ M.) at 368 nm displays a characteristic fluorescence spectrum for anthracene group with the most intensive band at 415 nm. The emission is slightly enhanced upon coordination of such metal ions as Ni²⁺ and Zn²⁺. However, much higher intensity of emission is obsd. in the case of Cu²⁺ complex. The fluorescence enhancement is presumably due to suppression of photoinduced fluorophore-to-metal electron-transfer mechanism.

A New Reverse PET Chemosensor and Its Chelatoselective Aromatic Cadmiation. Choi, Miwhoa; Kim, Mihyang; Lee, Kap Duk; Han, Kuk-Nyo; Yoon, In-A.; Chung, Hye-Jin; Yoon, Juyoung.

Department of New Materials Chemistry and Nanophotonics Research Center, Silla University, Pusan, S. Korea. *Organic Letters* (2001), 3(22), 3455-3457.

Abstract: A new fluorescent chemosensor, anthryl tetra acid, was synthesized and showed large fluorescence quenching effects in 100% aq. soln. with metal ions via photoinduced electron transfer (PET). Chelatoselective fluorescence perturbation was obsd. with Cd(II) and resulted from electrophilic arom. cadmiation.

A New Fluorescent Chemosensor for Copper Ions Based on Tripeptide Glycyl-Histidyl-Lysine (GHK). Zheng, Yujun; Huo, Qun; Kele, Peter; Andreopoulos, Fotios M.; Pham, Si M.; Leblanc, Roger M. Center for Supramolecular Science and Department of Chemistry, University of Miami, Coral Gables, FL, USA. *Organic Letters* (2001), 3(21), 3277-3280.

Abstract: A new fluorescent chemosensor for Cu²⁺ ions was synthesized by modifying the tripeptide glycyl-histidyl-lysine (GHK) with 9-carbonylanthracene via the std. Fmoc solid-phase peptide synthesis method. While significant fluorescence quenching was obsd. from the mol. upon binding with Cu²⁺, adn. of Fe²⁺, Co²⁺, Ni²⁺, and Zn²⁺ to the peptide soln. caused a min. fluorescence emission spectral change, indicating a high specificity of this chemosensor for Cu²⁺ ions. Effects of pH were also studied.

Preparation of a solid support for combinatorial fluorescent chemosensor arrays using optical fibers. Prince, Maureen J.; Kaltcheva, Nadejda T.; Prince, Barry J.; Geissinger, Peter; Schwabacher, Alan W. Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, WI, USA. Abstracts of Papers, 222nd ACS National Meeting, Chicago, IL, United States, August 26-30, 2001 (2001), ORGN-526. Publisher: American Chemical Society, Washington, D. C.

Abstract: We have recently described the advantages of solids supports of linear morphol. for combinatorial split/mix type synthetic parallelism with full spatial encoding. Here we present a novel prepn. of a versatile solid support for synthesis and assay in forms appropriate to linear spatially encoded combinatorial synthesis to directly yield a chemosensor array. Meldal's SPOCC resin is a stable, UV transparent, polyether support compatible with org. and aq. conditions. We describe convenient and novel prepn. methods to control the crosslink d. and functional loading of the resin. We also describe prepn. of the polymer as a film, on which localized compds. are directly assayed through use of optical fibers. We demonstrate an evanescent fiber-fiber coupling scheme for the probing of fluorescent mols. in a fiber cladding with high spatial resolu.

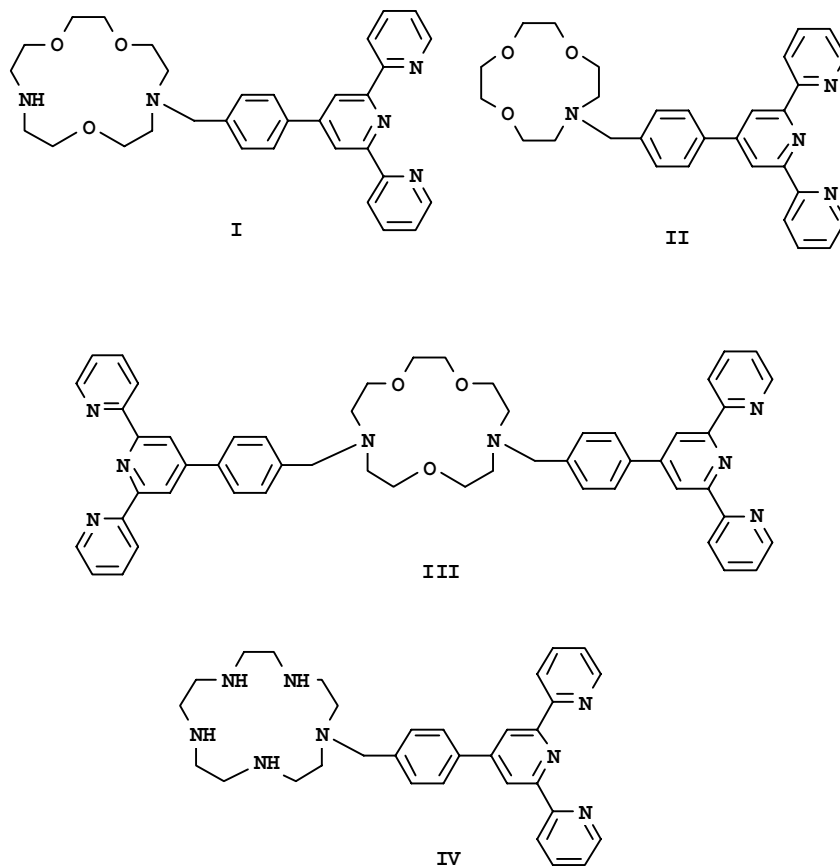
The chemosensor of immobilized fluorescent cyclodextrin for detecting molecules. Tanabe, T.; Touma, K.; Hamasaki, K.; Ueno, A. Department of Bioengineering, Faculty of Bioscience and Biotechnology, Tokyo Institute of Technology, Midori-ku, Yokohama, Japan. Cyclodextrin: From Basic Research to Market, International Cyclodextrin Symposium, 10th, Ann Arbor, MI, United States, May 21-24, 2000 (2000), 88-91. Publisher: Wacker Biochem Corp., Adrian, Mich

Abstract: Cyclodextrin form inclusion complexes with various org. mols. By now various fluorescent cyclodextrins were studied only in soln. The authors report here the newly immobilization method of the fluorescent cyclodextrin using a cellulose membrane and the mol. recognition ability of the membrane.

Fluorescent chemosensors for heavy metal ions based on bis(terpyridyl) ruthenium(II) complexes containing Aza-Oxa and polyaza macrocycles. Padilla-Tosta, Miguel E.; Lloris, Jose Manuel; Martinez-Manez, Ramon; Marcos, M. Dolores; Miranda, Miguel A.; Pardo, Teresa; Sancenon, Felix; Soto, Juan. Departamento de Quimica, Universidad Politecnica de Valencia, Valencia, Spain. *European Journal of Inorganic Chemistry* (2001), (6), 1475-1482. CODEN: EJICFO ISSN: 1434-1948. Journal written in English.

Abstract: Reactions of 4'-[4-(bromomethyl)phenyl]-2,2':6',2''-terpyridine with 4,10-diaza-15-crown-5 and 1-aza-12-crown-4 in CH₂Cl₂ yielded the ligands I (L1) and II (L3), resp. Reaction of an excess of 4'-[4-(bromomethyl)phenyl]-2,2':6',2''-terpyridine with 4,10-diaza-15-crown-5 yielded III (L2), while treatment of the same terpyridine ligand with 1,4,7,10,13-pentaazacyclopentadecane afforded IV (L4).

Reactions of L1, L3, and L4 with Ru(mtpy)Cl₃ (mtpy = 4'-methyl-2,2':6',2''-terpyridine) in MeOH yielded the metallo receptors [Ru(L1)(mtpy)][PF₆]₂, [Ru(L3)(mtpy)][PF₆]₂, and [Ru(L4)(mtpy)][PF₆]₂ after pptn. with ammonium hexafluorophosphate and column chromatog. On treating L3 with RuCl₃, the homoleptic Ru complex [Ru(L3)₂][PF₆]₂ was obtained. The synthesized metallo receptors contain oxa-aza crown or polyazacycloalkane moieties as recognition sites and [Ru(tpy)₂]²⁺ cores as the signal-generating center. The electronic spectra of the complexes are as expected for an Ru(tpy)₂²⁺ chromophore, with the main Ru[d(π) → tpy(π*)] MLCT transition at .apprx.484 nm and intense ligand-centered transitions in the UV region. One of the most interesting aspects of these Ru complexes is their multicomponent nature, as they contain both coordination sites and fluorescent Ru(tpy)₂²⁺ cores. [Ru(L1)(mtpy)]²⁺, [Ru(L3)(mtpy)]²⁺, and [Ru(L3)₂]²⁺ display an emission max. at .apprx.650 nm, the intensity of which is pH dependent, showing an enhancement upon protonation. The metallo receptor [Ru(L1)(mtpy)]²⁺ selectively senses Hg²⁺ in preference to Cu²⁺, Cd²⁺, and Pb²⁺. The emission intensity vs. pH curve for [Ru(L2)(mtpy)]²⁺ in the presence of Cu²⁺ and Hg²⁺ ions is close to that of the free receptor, but the presence of Cd²⁺ or Pb²⁺ enhances the emission intensity in the range pH 4-6. For the [Ru(L3)₂]²⁺ complex, Cd²⁺, Pb²⁺, and Hg²⁺ induce an enhancement of the fluorescence of the Ru(tpy)₂²⁺ core in the range pH 3.5-7.5. These results are compared with those obtained for the metallo receptor [Ru(L4)(mtpy)]²⁺ contg. a polyazacycloalkane moiety as the binding domain.



Dual-signaling fluorescent chemosensors based on conformational restriction and induced charge transfer. Mello, Jesse V.; Finney, Nathaniel S. Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA, USA. *Angewandte Chemie, International Edition* (2001), 40(8), 1536-1538.

Abstract: Biarylpyridines as dual-channel fluorescent chemosensors based on conformational

restriction and induced charge transfer were prepd. Appending the biarylpyridines with polyether metal binding domains leads to dual-channel fluorescent chemosensors that are remarkably responsive and selective given their structural simplicity.

Conformational restriction as a signal transduction mechanism for fluorescent chemosensors.

Finney, Nathaniel S.; McFarland, Sherri A.; Mello, Jesse V.; Fang, Albert. Department of Chemistry and Biochemistry, UCSD, La Jolla, CA, USA. Abstr. Pap. - Am. Chem. Soc. (2001), 221st ORGN-696.

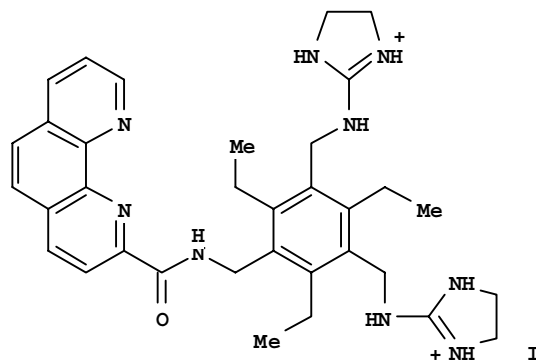
Abstract: Fluorescent chemosensors - mols. that change their fluorescence in response to substrate binding - offer an extremely sensitive optical method for the real-time monitoring of mol. interactions. Such chemosensors are finding increased use in fields as diverse as biol., medical anal., and environmental monitoring. Virtually all fluorescent chemosensors operate by one of three mechanisms: 1) suppression of photoinduced electron transfer or enhancement of heavy-atom quenching; 2) variation of the distance between two fluorophores, modulating the efficiency of inter-chromophore energy transfer; and 3) alteration of the micro-environment of a solvatochromic fluorophore (e.g. by displacement from a cyclodextrin cavity). We have explored an alternative mechanism for fluorescent chemosensor action, in which substrate binding leads to conformational restriction of a fluorophore, in turn producing fluorescence enhancement. Even simple systems based on this approach, such as those shown below, exhibit strong fluorescence enhancement and high binding selectivity.

Fluorescent chemosensors based on conformational restriction of a biaryl fluorophore. McFarland, Sherri A.; Finney, Nathaniel S. Department of Chemistry, UCSD, La Jolla, CA, USA. Abstr. Pap. - Am. Chem. Soc. (2001), 221st ORGN-168.

Abstract: Fluorescent chemosensors offer extremely sensitive optical method for the real-time monitoring mol. interactions. Such chemosensors are finding increased use in fields diverse as biol., medical anal., and environmental monitoring. Virtually all fluorescent chemosensors operate by one of three mechanisms: 1) suppression of photoinduced electron transfer 2) variation of the distance between two fluorophores and 3) alteration of the micro-environment of solvatochromic fluorophore. We describe here alternative mechanism for fluorescent chemosensor action, in which substrate binding leads to conformational restriction of biaryl fluorophore in turn producing fluorescence enhancement.

Metal triggered fluorescence sensing of citrate using a synthetic receptor. Cabell, Larry A.; Best, Michael D.; Lavigne, John J.; Schneider, Stephen E.; Perreault, Denise M.; Monahan, Mary-Katherine; Anslyn, Eric V. The Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX, USA. Journal of the Chemical Society, Perkin Transactions 2 (2001), (3), 315-323.

Abstract : A metal contg. fluorescent chemosensor was designed, synthesized, and studied for the quantification of citrate in common beverages. The sensor consists of Cu(II) bound by a 1,10-phenanthroline ligand which is attached to a bis(aminoimidazolium) receptor (I). Receptor I was designed such that binding of the metal creates an addnl. binding site for citrate. This addnl. binding interaction was found to increase the metal and citrate binding consts. in a cooperative manner, yielding a min. 2.0 fold increase in the citrate binding const. and a min. 2.0 fold increase in the Cu(II) binding const. Further, I was designed so that binding of Cu(II) quenches a photo-excited state of the 1,10-phenanthroline fluorophore. Thus, addn. of citrate to I-Cu(II) resulted in an increase of the fluorescence of the system. The nature of the fluorescence modulation upon citrate binding was probed using a model compd. (6-Cu(II)). The data support an increase of electron d. on the metal due to the donating ability of a carboxylate anion of citrate. In a sensing assay, the receptor is effective for measuring citrate concns. in the micromolar range in highly competitive media. The authors believe this is the first demonstration of anion sensing in which the fluorescence emission is modulated due to a perturbation in the metal quenching effect upon analyte binding.



Intramolecular excimer formation and complexing behavior of 1,n-bis(naphthalenecarboxy)oxaalkanes as fluorescent chemosensors for calcium and barium ions.

Kawakami, J.; Komai, Y.; Sumori, T.; Fukushi, A.; Shimozaki, K.; Ito, S. Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University, Aomori, Hirosaki, Japan. *Journal of Photochemistry and Photobiology, A: Chemistry* (2001), 139(1), 71-78.

Abstract: The photochem. and photophys. was studied of 1,n-Bis(1-naphthalenecarboxy)oxaalkanes (1NPnN, n = 1-6) and 1,n-bis(2-naphthalenecarboxy)oxaalkanes (2NPnN, n = 1-6). The authors studied the relationship between the length of the polyether chain and the metal ion recognition of NPnN (NPnN = 1NPnN or 2NPnN, n = 1-6) in acetonitrile soln., and the influence of the naphthalene substitution position (α -position or β -position) for metal ion recognition. Changes in the fluorescence spectra of NPnN (n = 1-3) were not obsd. by the addn. of alkali and alk. earth metal salts. However, the spectra of NPnN (n = 4-6) were changed by the addn. of calcium and barium salts. Esp. in NPnN (n = 5, 6), the changes in the shape and intensity of the fluorescence spectra were great. The values of log K for Ca²⁺ and Ba²⁺ were 2NP6N > 1NP6N > 2NP5N > 1NP5N. In the cases of same length of the polyether chain, 2NPnN is an excellent fluorescent chemosensor for Ca²⁺ and Ba²⁺, better than 1NPnN.

Cu²⁺-Induced Blue Shift of the Pyrene Excimer Emission: A New Signal Transduction Mode of Pyrene Probes. Yang, Jye-Shane; Lin, Che-Sheng; Hwang, Chung-Yu. Department of Chemistry, National Central University, Chung-Li, Taiwan. *Organic Letters* (2001), 3(6), 889-892.

Abstract: A pentyptycene-bispyrenyl system (1) was synthesized and studied as a fluorescent chemosensor for metal ions. A novel blue shift along with an intensity enhancement of the pyrene excimer emission is obsd. for 1 in the presence of Cu²⁺. Such a new signal transduction mode of pyrene probes results from the formation of a static pyrene excimer that has very different characteristics from its dynamic counterpart.

Bibliographic Information

Fluorescent chemosensors based on conformational restriction of a biaryl fluorophore. McFarland, Sherri A.; Finney, Nathaniel S. Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA, USA. *Journal of the American Chemical Society* (2001), 123(6), 1260-1261.

Abstract: A fluorescent chemosensor mechanism based on conformational restriction of fluorescent biaryl ethers is presented. Titrn. of the compds. with group I and II metal cations led to fluorescence enhancement at the emission maxima. The system is characterized by structural simplicity and strong, selective fluorescence response to metal binding. UV absorption spectra did not indicate a change in the degree of ground-state planarity .

Bibliographic Information

A new fluorescent chemosensor: synthesis and molecular recognition by sulfamidopyrrolidinylidene

modified β -cyclodextrin. Reddy, L. Rajender; Reddy, M. Arjun; Bhanumathi, N.; Rao, K. Rama. Org. Chem. Div.-I, Indian Inst. Chem. Technol., Hyderabad, India. Journal of Chemical Research, Synopses (2000), (10), 494-495.

Abstract: The prepn. of title cyclodextrin inclusion complexes with cholic acid is reported. Mono[6-deoxy-6-(1-methyl-2-pyrrolidinylidene-sulfamido)]- β -cyclodextrin synthesized as new artificial receptor has shown mol. recognition with remarkable sensitivity to various org. compds. with variation of fluorescence upon guest binding.

Bibliographic Information

Ion-specific aggregation in conjugated polymers: highly sensitive and selective fluorescent ion chemosensors. Kim, Jinsang; McQuade, D. Tyler; McHugh, Sean K.; Swager, Timothy M. Dep. Chem., Massachusetts Inst. Technology, Cambridge, MA, USA. Angewandte Chemie, International Edition (2000), 39(21), 3868-3872.

Abstract: A new transduction mechanism based on the aggregation of conjugated sensory polymers induced by K^+ ions is reported; this new system displays enhanced sensitivity because of energy migration processes and has a high selectivity for K^+ over Na^+ ions. The poly(p-phenylene ethynylene)s were synthesized by the Sonogashira-Hagihara coupling reaction.

Bibliographic Information

Fluorescent chemosensor for saturated hydrocarbons and other petroleum-related molecules. Its application using a chromatographic system: Berberine-induced fluorescence detection. Cebolla, Vicente L.; Membrado, Luis; Domingo, Maria P.; Cossio, Fernando P.; Arrieta, Ana; Vela, Jesus. Instituto de Carboquimica, CSIC, 50015 Zaragoza, Spain. Abstr. Pap. - Am. Chem. Soc. (2000), 220th PETR-036.

Abstract: Satd. hydrocarbons have traditionally been considered inert mols. Their detection with spectroscopic techniques has scarcely been investigated because they do not have UV or fluorescence spectra under anal. working conditions. Berberine cation allows satd. hydrocarbons (alkanes and cycloalkanes) to be detected and quantified with a high sensitivity. Other petroleum-related mols. (e.g., certain aroms.) can also be detected. This phenomenon can be adapted to TLC-Scanning Densitometry for compositional anal. of petroleum products. Computational calens. have demonstrated that this increase in fluorescence signal involves a weak, although anal. useful, electrostatic interaction between the corresponding alkane and the electron-deficient system of berberine cation. This is the first time that an explanation based on mol. interactions involving n-alkanes is proposed for explaining the nature of fluorescence enhancement without apparent chem. reaction.

Bibliographic Information

Fluorescent chemosensor for lanthanide ions. Xia, Wen-Sheng; Schmehl, Russell H.; Li, Chao-Jun. Department of Chemistry, Tulane University, New Orleans, LA, USA. Abstr. Pap. - Am. Chem. Soc. (2000), 220th ORGN-018.

Abstract: The synthesis and photophys. behavior of a luminescent chemosensor for the early lanthanide elements is described. The sensor is a 1,4-diphenylethynyl benzene chromophore having 18-crown-6 moieties bound to the outer Ph rings. The chromophore is luminescent and the emission is quenched by La^{3+} ions with larger ionic radii and existing f-f transitions (Ce^{3+} , Pr^{3+} and Nd^{3+}). Alkali, alk. earth ions and lanthanides with smaller radii (Ge^{3+} , Tb^{3+} , Dy^{3+} , Yb^{3+}) do not affect the emission.

Bibliographic Information

Synthesis of polymeric fluorescent chemosensor for the recognition of Fe^{3+} Ion. Yang, Changduk; Lee, Taek Seung. Department of Textile Engineering, College of Engineering, Chungnam National University, Taejon, S. Korea. Molecular Crystals and Liquid Crystals Science and Technology, Section A: Molecular Crystals and Liquid Crystals (2000), 349 283-286.

Abstract: The authors synthesized a polymer with acridine group in its main chain and found that the polymer soln. showed spectrometric and fluorometric changes upon addn. of ferric ion (Fe^{3+}) specifically

indicating that the polymer would be a useful sensing material for ferric ion.

Bibliographic Information

Fluorescent chemosensors containing polyamine receptors. Pina, Fernando; Bernardo, M. Alexandra; Garcia-Espana, Enrique. Departamento de Quimica, Centro de Quimica Fina e Biotecnologia, Universidade Nova de Lisboa, Monte de Caparica, Port. European Journal of Inorganic Chemistry (2000), (10), 2143-2157.

Abstract: A review, with 45 refs., on development and use of chemosensors in scientific fields such as environmental chem., medicine, and processing and storage of information. Mol.-scale devices have the advantage of working on the same spatial scale as the chem. structures that are responsible for macroscopic behavior obsd. in the environment or those assocd. with health problems, and they allow the construction of mol.-scale devices for information storage. A family of chemosensors based on a polyamine receptor, e.g., tetraaza-paracyclophanes, N,N'-dibenzylated polyamines, polyamines contg. anthracene fluorophore or phenanthroline chromophore, and a fluorescent signaling unit is described. Polyamine receptors are water-sol. ambidentate receptors; they are able to coordinate either metal ions, e.g., Zn, Cd, Cu, when sufficient deprotonated amino groups are available, or anionic species or nucleotides, when there are sufficient protonated amino groups. The use of fluorescent signaling units confers the advantage of an immediate visual response/signal, in, e.g., mol. logic gates and metal scorpionate complex based mol. machines.

Bibliographic Information

Molecular recognition directed porphyrin chemosensor for selective detection of nicotine and cotinine. Deviprasad, Gollapalli R.; D'Souza, Francis. Dep. Chem., Wichita State University, Wichita, KS, USA. Chemical Communications (Cambridge) (2000), (19), 1915-1916.

Abstract: The first example of a metalloporphyrin based fluorescent chemosensor for selective detection of dinitrogen alkaloids such as nicotine and cotinine in soln. by using a 'two-point' binding strategy and a modified fluorescence anal. procedure is reported.

Bibliographic Information

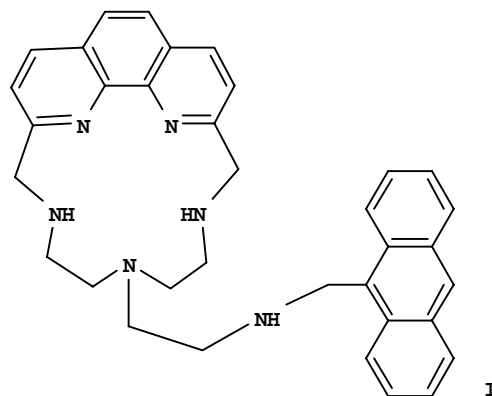
A simple fluorescent chemosensor for alkaline-earth metal ions. Prodi, L.; Ballardini, R.; Gandolfi, M. T.; Roversi, R. Dipartimento di Chimica 'G. Ciamician', Universita di Bologna, Bologna, Italy. Journal of Photochemistry and Photobiology, A: Chemistry (2000), 136(1-2), 49-52.

Abstract: In acetonitrile solns., the deprotonated form of 1-pyrenebutyric acid (1) forms 1:2 (metal:ligand) complexes with Zn²⁺, Cu²⁺, Fe²⁺, Fe³⁺, and alk. earth metal ions. The complexation process leads two pyrene moieties in close contact, so that dimers are formed, causing strong changes in the absorption and fluorescence spectra. Taking advantage of these changes, very low concns. of alk. earth metal ions can be detected, suggesting 1 as a good prototype of a new family of fluorescent sensors.

Bibliographic Information

A novel fluorescent chemosensor exhibiting exciplex emission. An example of an elementary molecular machine driven by pH and by light. Bencini, Andrea; Bianchi, Antonio; Masotti, Andrea; Valtancoli, Barbara; Lodeiro, Carlos; Parola, A. Jorge; Pina, Fernando; de Melo, J. Seixas. Dep. Chem., University of Florence, Florence, Italy. Chemical Communications (Cambridge) (2000), (17), 1639-1640.

Abstract: Coordination/detachment of a pendent functionality in the Zn(II) complex with a macrocyclic ligand contg. phenanthroline and pendant anthracene moieties gives rise to on/off switching of exciplex emission, defining an elementary mol. machine whose movements are driven by both pH and light. The fluorescence of I and its zinc complexes is quenched at pH values where its nitrogens are neither coordinated to zinc nor protonated. π -Stacking of the anthracene and phenanthroline occurs due to a change in the zinc coordination environment and is driven by light and pH.



Bibliographic Information

A polymer having pendent α -aminoanthracene groups as a fluorescent chemosensor. Kim, Jong-Man; Chang, Tae-Eun; Han, Dong Keun; Ahn, Kwang-Duk. Molecular Engineering Laboratory, Life Sciences Division, Korea Institute of Science and Technology, Seoul, S. Korea. *Journal of Photopolymer Science and Technology* (2000), 13(2), 273-276.

Abstract: Methacrylate monomer contg. α -aminoanthracene as a fluorescent chemosensor was prepd. and polymd. with Me methacrylate to give a copolymer. The strong fluorescence emission of the polymer at 430 nm was effectively restored in the presence of acids by protonation and the degree of the increase in fluorescence intensity was dependent on the strength of the acid used.

Bibliographic Information

A fluorescent chemosensor for saturated hydrocarbons and other petroleum-related molecules - its application using a chromatographic system: berberine-induced fluorescence detection. Cebolla, Vicente L.; Membrado, Luis; Domingo, Maria P.; Cossio, Fernando; Arrietu, Ana; Fakultatea, Kimika; Vela, Jesus. Instituto Carboquimica, CSIC, Zaragoza, Spain. *Preprints - American Chemical Society, Division of Petroleum Chemistry* (2000), 45(4), 577-579.

Abstract: Satd. hydrocarbons have traditionally been considered inert mols. Their detection with spectroscopic techniques has scarcely been investigated because they do not have UV or fluorescence spectra under anal. working conditions. However, when berberine sulfate is in the presence of a satd. hydrocarbon (e.g., on a silica gel layer), and the system is irradiated with long-wave UV light, a fluorescent signal was found to be produced, the intensity of which depends on the hydrocarbon concn. and structure. Therefore, berberine sulfate is a fluorescent sensor for satd. hydrocarbons.

Bibliographic Information

Method for screening peptides for metal coordinating properties and fluorescent chemosensors derived therefrom. Imperiali, Barbara; Walkup, Grant K. (California Institute of Technology, USA). U.S. (2000), 19 pp.

Abstract: Methods for identifying polypeptides which coordinate to select metals, chemosensors comprising polypeptides which coordinate to select metals and methods for selectively detecting the presence of metals using these chemosensors are disclosed.

Bibliographic Information

Fluorescent Chemosensor for Metal Cations Based on Thiacalix[4]arenes Modified with Dansyl Moieties at the Lower Rim. Higuchi, Y.; Narita, M.; Niimi, T.; Ogawa, N.; Hamada, F.; Kumagai, H.; Iki, N.; Miyano, S.; Kabuto, C. Tegata, Faculty of Engineering and Resource Science, Department of Materials-Process Engineering and Applied Chemistry for Environments, Akita University, Akita, Japan.

Tetrahedron (2000), 56(27), 4659-4666.

Abstract: The selective de-tert-butylation of p-tert-Bu thiacalix[4]arene (p-tert-Bu TCA) with AlCl₃ at 80° was studied. Mono-, di-, and tri-p-tert-Bu thiacalix[4]arene (mono-, di- and tri-TCA, resp.) were obtained in yields of 6.5, 20 and 21%, resp., when p-tert-Bu TCA was treated with 7.1 equiv of AlCl₃ for 30 min. De-tert-Bu TCA was exclusively obtained when 10.5 equiv of AlCl₃ was used. These derivs. are converted to fluorescent active derivs. by modification with dansyl moiety at the lower rim, which were used as metal sensors in aq. soln. The extent of the fluorescent variations with the metal cations was used to display the sensing factors, $\Delta I/I_0$. These hosts show much higher sensitivity for transition metal cations such as Co²⁺, Ni²⁺, and Cd²⁺ than those of alkali metal cations such as Li⁺, Na⁺, and K⁺. The effect of p-tert-Bu groups on metal sensing ability of these hosts was studied. P-tert-Bu groups decrease the sensing ability of these hosts. It is the 1st example to show that water sol. TCA derivs. can detect metal cations directly in aq. soln. by variation of fluorescence intensity upon addn. of a metal cation.

Bibliographic Information

An Effective Fluorescent Chemosensor for Mercury Ions. Prodi, Luca; Bargossi, Carlotta; Montalti, Marco; Zaccheroni, Nelsi; Su, Ning; Bradshaw, Jerald S.; Izatt, Reed M.; Savage, Paul B. Dipartimento di Chimica G. Ciamician, Università di Bologna, Bologna, Italy. Journal of the American Chemical Society (2000), 122(28), 6769-6770.

Abstract: An ion-selective ligand based 5-nitro-8-hydroxyquinoline moieties attached to N atoms of diazacrown ether through a methylene group as a fluorescent chemosensor for Hg²⁺ is reported. The ligand displays good sensitivity, affinity, and selectivity for Hg²⁺ in a very large pH window (>2 pH units).

Bibliographic Information

Berberine cation: A fluorescent chemosensor for alkanes and other low-polarity compounds. An explanation of this phenomenon. Cossio, Fernando P.; Arrieta, Ana; Cebolla, Vicente L.; Membrado, Luis; Vela, Jesus; Garriga, Rosa; Domingo, Maria P. Kimika Fakultatea, Euskal Herriko Unibertsitatea, San Sebastian-Donostia, Spain. Organic Letters (2000), 2(15), 2311-2313.

Abstract: Alkanes in the presence of berberine sulfate provide an enhancement of fluorescent signal, which depends on alkane concn. and structure, when the system is irradiated with monochromatic UV light. Computational anal. suggests that an ion-induced dipole between alkanes and berberine sulfate is responsible for this phenomenon. This interaction can properly model the exptl. obtained fluorescent response. The proposed explanation allows other interacting systems to be designed, which were exptl. confirmed.

Bibliographic Information

Fluorescent chemosensor for metal ions using a polymer having pendant pyridylbenzoxazole groups. Kim, Jong-Man; Chong, Byong-Oh; Park, Ki Hong; Chang, Tae-Eun; Han, Dong Keun; Choo, Dong Joon; Ahn, Kwang-Duk. Functional Polymer Laboratory, Korea Institute of Science and Technology, Seoul, S. Korea. Polymer Bulletin (Berlin) (2000), 44(1), 79-84.

Abstract: A polymer having fluorescent pyridylbenzoxazole groups was prepd. for the purpose of detecting of metal ions. Metal ions such as Co²⁺, Ni²⁺, Cu²⁺ and Fe²⁺ coordinate with the bipyridyl-like fluorescent benzoxazole chromophores. Among the metal ions studied, the Fe²⁺ ion is the most effective in terms of its fluorescence quenching ability. The addn. of a metal scavenger 2,2'-dipyridyl to the metal ion-quenched polymer soln. resulted in the recovery of the fluorescence.

Bibliographic Information

Synthesis and molecular recognition properties of a novel chemical modified β -cyclodextrin. Xie, Hongzhi; Wang, Pengfei; Wu, Shikang. Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing, Peop. Rep. China. Progress in Natural Science (2000), 10(1), 27-32.

Abstract: A new fluorescent chemosensor, a kind of β -cyclodextrin (CD) modified with N',N'-dimethylaminochalcone, was synthesized. The photophys. behavior and the mol. recognition of this compd. were investigated by fluorescence spectroscopy. The results show that there exists an "in-out"

movement of appended chalcone group from cyclodextrin cavity for "large dimension guest mol." such as 1-adamantanecarboxylic acid. But the long-chained guests such as cationic surfactants can be inserted into the CD cavity as a spacer to form a ternary inclusion complex with the CD cavity and the chalcone moiety.

Bibliographic Information

Transition-metal modulated excited-state dynamics in highly sensitive, fluorescent chemosensor materials. Jones, Wayne E., Jr.; Zhang, Yan; Murphy, Clifford; Chatterjee, Sudipta; Seok, Elizabeth; King, Brian. Chemistry Department and Institute for Materials Research, SUNY, Binghamton, NY, USA. Book of Abstracts, 219th ACS National Meeting, San Francisco, CA, March 26-30, 2000 (2000), ORGN-786. Publisher: American Chemical Society, Washington, D. C

Abstract: Conjugated fluorescent polymers have recently found use in a variety of chemosensor applications. We have prepd. a conjugated polyphenylenethiophene structure with pendant Lewis base binding sites suitable for binding transition metal ions in org. or aq. soln. Initial investigations reveal nM sensitivity to several metals that are toxic to the environment including Ni(II), Hg(II), and Pb(II). Stern-Volmer investigations of the resulting fluorescence quenching show a strong upward curvature indicating a combination of both static and dynamic quenching pathways. Careful spectroscopic anal. suggests that ligand field deactivation paths at the metal may play a dominant role in this highly efficient quenching process. By tuning the ligand field states and low lying metal to ligand charge transfer states, it may be possible to further optimize these new fluorescent chemosensor materials. Thin films of these and related polymer thin films prepd. by self-assembly can also be used to enhance selectivity.

Bibliographic Information

Dendrimers as fluorescent sensors with signal amplification. Balzani, Vincenzo; Ceroni, Paola; Gestermann, Sven; Kauffmann, Christopher; Gorka, Marius; Vogtle, Fritz. Dip. Chim. "G. Ciamician", Universita di Bologna, Bologna, Italy. Chemical Communications (Cambridge) (2000), (10), 853-854.

Abstract: In a 4th generation poly(propylene amine) dendrimer decorated with 32 dansyl units at the periphery and contg. 30 aliph. amine units in the interior, the strong fluorescence of all the dansyl units is quenched when a Co²⁺ ion is incorporated into the dendrimer.

Bibliographic Information

A novel cesium selective fluorescent chemosensor. Xia, Wen-Sheng; Schmehl, Russell H.; Li, Chao-Jun. Dep. Chem., Tulane University, New Orleans, LA, USA. Chemical Communications (Cambridge) (2000), (8), 695-696.

Abstract: A novel Cs selective fluorescent chemosensor was designed and synthesized; the chemosensor exhibited a selective fluorescent enhancement in the presence of other alkali metal ions.

Bibliographic Information

Peptide platforms for metal ion sensing. Imperiali, Barbara; Pearce, Dierdre A.; Sohna Sohna, Jean-Ernest; Walkup, Grant; Torrado, Alicia. Div. Chem. Chem. Eng., California Institute of Technology, Pasadena, CA, USA. Proceedings of SPIE-The International Society for Optical Engineering (1999), 3858(Advanced Materials and Optical Systems for Chemical and Biological Detection), 135-143.

Abstract: A review, with 31 refs. Naturally occurring motifs were redesigned to produce fluorescent peptidyl-chemosensors that sensitively and selectively recognize Cu(II) or Fe(III). The modular nature of peptide architecture allows prepn. and evaluation of potential sensors on solid supports.

Bibliographic Information

Synthesis and study of a molecular fluorescent chemosensor for potassium. Xia, Wen-Sheng; Schmehl, Russell H.; Li, Chao-Jun. Department of Chemistry, Tulane University, New Orleans, LA, USA. European Journal of Organic Chemistry (2000), (3), 387-389.

Abstract: A potassium selective fluorescent chemosensor was designed and synthesized. The mol.

sensor is weakly luminescent in acetonitrile soln., but exhibits a significant increase in intensity upon addn. of K⁺. The luminescence intensity increases reach a plateau when the K⁺/chemosensor ratio is 3:2. The sensor shows a linear fluorescent enhancement with the concn. of potassium ion in the presence of a large excess of sodium ion.

Bibliographic Information

A fluorescent chemosensor based on a ruthenium(II)-terpyridine core containing peripheral amino groups that selectively sense ATP in an aqueous environment. Padilla-Tosta, M. E.; Lloris, J. M.; Martinez-Manez, R.; Pardo, T.; Soto, J.; Benito, A.; Marcos, M. D. Departamento de Quimica, Universidad Politecnica de Valencia, Valencia, Spain. *Inorganic Chemistry Communications* (2000), 3(1), 45-48.

Abstract: The selective sensing of the ATP anion in an aq. environment over phosphate, sulfate, and chloride using a fluorescence chemosensor based on Ru(tpy)₂²⁺ cores attached to polyammonium groups is reported.

Bibliographic Information

Lariat ethers with pendant phenanthridine units. Synthesis and complexation of Na- and K-picrate. Alihodzic, Sulejman; Zinic, Mladen. Laboratory for Supramolecular and Nucleoside Chemistry, Department of Organic Chemistry and Biochemistry, Rudjer Boskovic Institute, Zagreb, Croatia. *Croatia Chemica Acta* (1999), 72(4), 803-817.

Abstract: Lariat ethers with appended phenanthridine fluorophoric units were prepd. as potential fluorescent chemosensor mols. for alk. metal salts possessing arom. anions. The starting 8-ethyloxycarbonylamino-6-methylphenanthridine was converted to N-(2-tosylethyl) derivs. suitable for N-alkylation of diaza- and aza-18-crown-6. However, the alkylation failed, giving a 2-oxazolidinone deriv. formed by intramol. cyclization of phenanthridine N-carbamate intermediates under basic conditions. A phenanthridine deriv. having benzyl instead carbamate protection on the 8-amino group was successfully alkylated using mono- and diaza-crown ethers, giving lariat ethers. Subsequently, benzyl protective groups were removed under acidic conditions. One of the target lariat ethers was found to form unique Na- and K-picrate complexes with the metal cation bound in the crown cavity and picrate anion intercalated between phenanthridine units.

Bibliographic Information

Action of a fluorescent chemosensor for Cu²⁺ encapsulated in silica xerogel. Klonkowski, A. M.; Kledzik, K.; Ostaszewski, R. Faculty of Chemistry, University of Gdansk, Gdansk, Pol. *Journal of Inclusion Phenomena and Macrocyclic Chemistry* (1999), 35(1-2), 165-171.

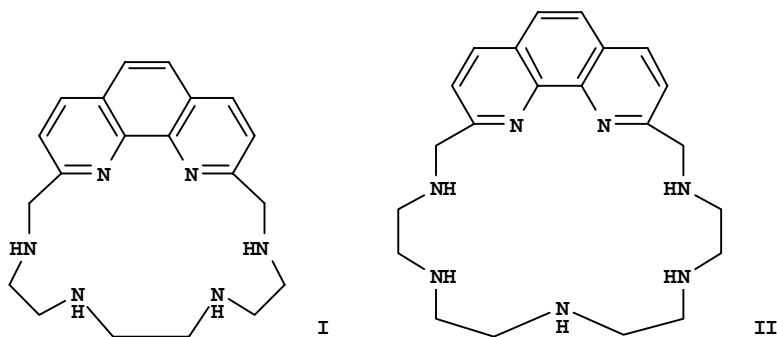
Abstract: The fluorescent chemosensor Ant-NH-O-O-NH-Ant for Cu²⁺ ions was designed by a supramol. approach, as follows: two anthracene (Ant) fragments as fluorophore subunits were linked by a noncyclic NH-O-O-NH quadridentate ligand as a receptor. The interaction of Cu²⁺ - receptor is signaled through the enhancement of the anthracene fluorescence when the receptor, i.e., the dioxodiamine chain subunit of the sensor is able to stop a photoinduced electron-transfer mechanism. The expts. with the chemosensor encapsulated in silica xerogel by the sol-gel processing are described.

Bibliographic Information

Macrocyclic polyamines containing phenanthroline moieties. Fluorescent chemosensors for H⁺ and Zn²⁺ ions. Bencini, Andrea; Bernardo, M. Alexandra; Bianchi, Antonio; Fusi, Vieri; Giorgi, Claudia; Pina, Fernando; Valtancoli, Barbara. Department Chemistry, Univ. Florence, Florence, Italy. *European Journal of Inorganic Chemistry* (1999), (11), 1911-1918.

Abstract: The macrocyclic ligands I and II, contg. a triethylenetetraamine and a tetraethylenepentaamine moiety linked to the Me groups of 2,9-dimethyl-1,10-phenanthroline, bind H⁺ and Zn²⁺ ions giving rise to modulation of the fluorescence emission intensity. The equil. const. and the enthalpy changes for ligand protonation were detd. by means of pH-metric and microcalorimetric methods in 0.1 M Me₄NCl solns. at 298.1 ± 0.1 K. Also the stability const. of the Zn²⁺ complexes were detd.

under the same exptl. conditions. Compd. I forms only mononuclear complexes, while II also forms dizinc(II) species. The phenanthroline group has fluorescence emission properties, but interaction with the lone pairs of benzylic N atoms produces an efficient quenching of the emission. Such a quenching effect can be avoided by deactivation of the benzylic N atoms by protonation or Zn²⁺ complexation. Hence, I and II behave as chemosensor for H⁺ and Zn²⁺, the photochem. properties of the ligands being modulated by the formation of different protonated and complexed species. In the case of II, the fluorescence emission is also controlled by the metal to ligand molar ratio, because of the formation of an emissive binuclear complex.



Bibliographic Information

Fluorescent chemosensor for carbohydrates which shows large change in chelation-enhanced quenching. Adhikiri, Devi P.; Heagy, Michael D. Department of Chemistry, New Mexico Institute of Mining and Technology, Socorro, NM, USA. *Tetrahedron Letters* (1999), 40(45), 7893-7896.

Abstract: A new water-sol. saccharide receptor based on a naphthalic anhydride fluorophore was synthesized from 3-aminophenylboronic acid. The large change in fluorescence intensity ($I/I_0 = \text{ca. } 0.25$) and measured pK_a (7.7) make this compd. a useful chemosensor at neutral pH.

Bibliographic Information

Preparation and immobilization of 6-amino-2,3-di(2-pyridyl)quinoxaline. New fluorescent chemosensory materials for heavy metal ions. Kanbara, Takaki; Takakusagi, Hitoshi; Kagaya, Shigehiro; Hasegawa, Kiyoshi. Department of Chemical and Biochemical Engineering, Faculty of Engineering, Toyama University, Toyama, Japan. *Chemistry Letters* (1999), (9), 969-970.

Abstract: 6-Amino-2,3-di(2-pyridyl)quinoxaline and its derivs. were synthesized and immobilized to polymer support, and the interaction with metal ions was examd. The spectroscopic data predict promising chemosensory materials.

Bibliographic Information

Complexing behavior of new naphthalene derivatives having amide groups as fluorescent chemosensors for alkali and alkaline earth metal ions. Kawakami, Jun; Fukushi, Atsuo; Ito, Shoei. Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University, Aomori, Japan. *Chemistry Letters* (1999), (9), 955-956.

Abstract: New naphthalene derivs. (1NSN, 1NLN, 1NE and 1NcrownN) as fluorescent chemosensors for metal ions using excimer emission were synthesized. The authors studied the metal ion recognition of 1NSN, 1NLN, 1NE and 1NcrownN. Large changes in the fluorescence spectra of not only 1NSN and 1NLN but also 1NE were obsd. with the addn. of Mg ion. However, changes in the fluorescence spectra of 1NcrownN were not obsd. with the addn. of alkali and alk. earth metal ions.

Bibliographic Information

Fluorescent chemosensors for metal ion recognition by means of naphthalene derivatives.

Kawakami, Jun; Komai, Yuko; Sumori, Tadashi; Sata, Hirohito; Ito, Shoei. Department of Chemistry, Faculty of Science, Hirosaki University, Hirosaki, Japan. *Recent Research Developments in Pure & Applied Chemistry* (1998), 2(Pt. 2), 231-237.

Abstract: 1,N -Bis(1- or 2-naphthalenecarboxy)oxaalkanes (1NPnN, 2NPnN, n = 1-6) and 1-(1-naphthalene carboxy)-n-(p-substituted benzenecarboxy) oxaalkanes (1NPnX, X=Me, H, Cl, CF₃, CN, n = 1-6) as fluorescent sensors by excimer or exciplex emission for metal ions were synthesized, and the complexation them with alkali and alk. earth metal ions in acetonitrile was studied. Alk. earth metal cations suppress or enhance the fluorescence remarkably, depending on the cation size and the length of polyether chain.

Bibliographic Information

Fluorescent chemosensors for alkaline earth metal ions. Prodi, Luca; Bolletta, Fabrizio; Montalti, Marco; Pivari, Silvia; Zaccheroni, Nelsi. Dipartimento di Chimica "G. Ciamician", Universita di Bologna, Bologna, Italy. Editor(s): Di Natale, Corrado; D'Amico, Arnaldo; Sberveglieri, Giorgio. *Sensors and Microsystems, Proceedings of the Italian Conference*, 3rd, Genova, Feb. 11-13, 1998 (1999), Meeting Date 1998, 77-82. Publisher: World Scientific, Singapore, Singapore

Abstract: The group is actually involved in the synthesis and characterization of new fluorescent chemosensors, in which mol. recognition is accompanied by the switching on/off of a luminescence signal. The versatility of luminescence measurements makes these mols. suitable for building up electronic noses and tongues, representing a promising soln. to complex anal. problems. The authors report the more recent examples of chemosensors characterized by the group.

Bibliographic Information

Anthracene-linked calix[4]pyrroles: fluorescent chemosensors for anions. Miyaji, Hidekazu; Anzenbacher, Pavel, Jr.; Sessler, Jonathan L.; Bleasdale, Ellen R.; Gale, Philip A. Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX, USA. *Chemical Communications (Cambridge)* (1999), (17), 1723-1724.

Abstract: Fluorescent anthracene-calix[4]pyrrole conjugates were synthesized; these receptors can detect the presence of anions (e.g. F⁻, Cl⁻, H₂PO₄⁻) by a significant quenching of their fluorescence.

Bibliographic Information

Synthesis and Solution Structure Analysis of a Bispyrenyl Bishydroxamate Calix[4]arene-Based Receptor, a Fluorescent Chemosensor for Cu²⁺ and Ni²⁺ Metal Ions. Bodenant, Bruno; Weil, Tanja; Businelli-Pourcel, Magali; Fages, Frederic; Barbe, Bernard; Pianet, Isabelle; Laguerre, Michel. LCOO UMR 5802 CNRS, Universite Bordeaux 1, Talence, Fr. *Journal of Organic Chemistry* (1999), 64(19), 7034-7039.

Abstract: A bispyrenyl calix[4]arene-based receptor, 1, incorporating two hydroxamic acid functionalities was designed for the optical detection of Cu²⁺ and Ni²⁺ metal ions in soln. The synthetic route is based on the use of pyrene-labeled, O-protected hydroxylamines that represent versatile building blocks for the generation of fluorescent siderophore-based chelators. Compd. 1 is shown to exist in CDCl₃ soln. at room temp. as a mixt. of mainly two conformers, namely, the cone and partial-cone species (partial-cone/cone ratio .apprx.57/43). The full assignment of the proton and C resonances of the calix[4]arene core for both conformers is described. Ligand 1 exhibited in soln. a dual fluorescence emission spectrum composed of monomer and excimer contributions, the latter resulting from intramol. interactions between pyrene nuclei in the excited state. In MeOH/H₂O (80/20 vol./vol.), the fluorescence intensity is sensitive to proton concn. and to the presence of transition-metal ions. Addn. of Cu²⁺ and Ni²⁺ metal cations induced a dramatic quenching of fluorescence of 1 depending on the value of -log[H⁺]. The excimer-forming photoresponsive ligand 1 belongs to a new class of sensitive chemosensors for the selective detection of transition-metal species in aq. media.

Bibliographic Information

Novel fluorescent chemosensor for Li⁺ based on a squarylium dye carrying a monoazacrown moiety.

Kim, Sung-Hoon; Han, Sun-Kyung; Park, Sang-Hyun; Yoon, Cheol-Min; Keum, Sam-Rok. Department of Dyeing and Finishing, College of Engineering, Kyungpook National University, Taegu, S. Korea. *Dyes and Pigments* (1999), 43(1), 21-25.

Abstract: A squarylium dye carrying a monoazacrown moiety has been synthesized and characterized. The dye demonstrates sensitivity to Li^+ complexation with spectroscopic changes in fluorescence. Complex formation of the dye with Cu^{2+} was also investigated by UV-visible spectrometry.

Bibliographic Information

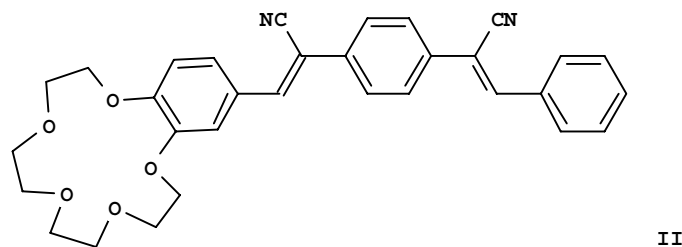
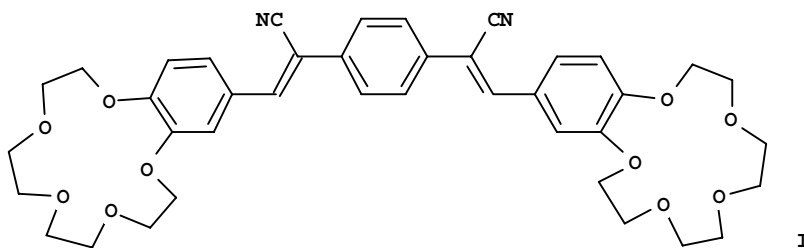
Intramolecular exciplex formation and complexing behavior of naphthalene derivatives as fluorescent chemosensors for calcium and barium ions. Kawakami, Jun; Itoh, Hiroyuki; Mitsuhashi, Haruki; Ito, Shoei. Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University, Hirosaki, Japan. *Analytical Sciences* (1999), 15(7), 617-618.

Abstract: The authors synthesized 1-(2-naphthalenecarboxy)-n-(p-cyanobenzenecarboxy)oxaalkanes (2NPnCN, n = 4-6) and 1-(1-naphthalenecarboxy)-n-(m-cyanobenzenecarboxy)oxaalkanes (1NPnCNm, n = 4-6), and studied the influence of the position of substituted naphthalene (a-position or f-position) and of the cyano group (para or meta) for metal-ion recognition. The authors now wish to report on the preliminary results of their study concerning metal-ion recognition by using 2NPnCN and 1NPnCNm. The fluorescence spectra of the naphthalene derivs. and their calcium complexes are given.

Bibliographic Information

A Highly Selective Fluorescent Chemosensor for K^+ from a Bis-15-Crown-5 Derivative. Xia, Wen-Sheng; Schmehl, Russell H.; Li, Chao-Jun. Department of Chemistry, Tulane University, New Orleans, LA, USA. *Journal of the American Chemical Society* (1999), 121(23), 5599-5600. CODEN: JACSAT ISSN: 0002-7863. Journal written in English.

Abstract: Compd. (I) is used as an excellent sensor material because of the sensitivity of fluorescence detection and selectivity to K^+ which is often difficult to detect due to the competition with Na^+ , which is generally present in much larger concn. in biol. systems such as human serum. Its analog compd. (II) is prep'd. and compared with compd. I. Compd. II which has only single crown exhibits no change in luminescence intensity upon addn. of both Na^+ and K^+ .



Bibliographic Information

Isolation of bright blue fluorescent substances from sonochemical hydroxylation of methyl p-cyanobenzoate. Yamada, Sachiko; Hokari, Hajime; Akasaka, Shinji; Iwamura, Michiko. Department

of Biomolecular Science, Faculty of Science, University of Toho, Chiba, Japan. *Chemistry Letters* (1999), (3), 197-198.

Abstract: Sonochem. hydroxylation of Me p-cyanobenzoate (1a) in water gave a bright blue fluorescence, which are mainly ascribed to three new fluorescent compds., 3-hydroxy, 2,3- and 2,5-dihydroxy derivs. of 1a. Other benzenes substituted with electron-withdrawing groups also gave similar fluorescence from their hydroxylated derivs. Among the fluorescence substances, Me 2,5-dihydroxybenzoate was supposed to be applicable for a fluorescent chemosensor.

Bibliographic Information

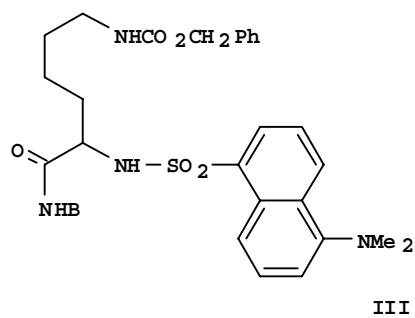
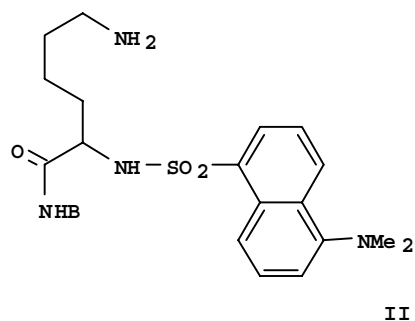
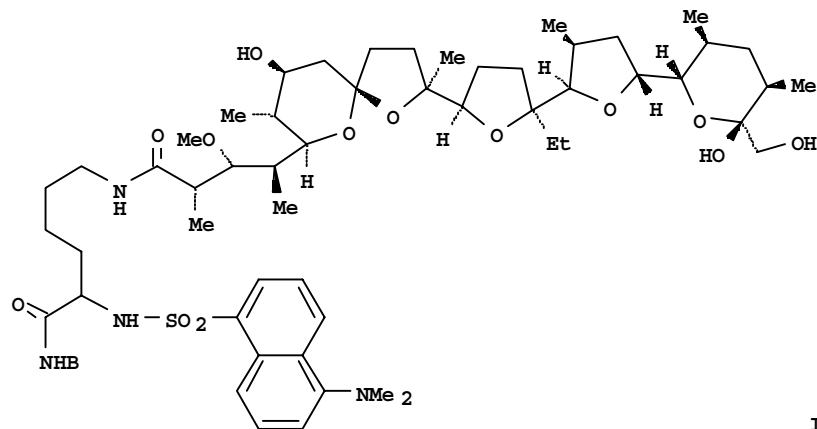
Tripodal coordination complexes as scaffolds for molecular recognition and catalysis. Canary, J. W.; Allen, C. S.; Castagnetto, J. M.; Chuang, C.-L.; Lajmi, A. R.; Santos, O. Dos; Xu, X. Department of Chemistry, New York University, New York, NY, USA. Editor(s): Coleman, Annette W. *Molecular Recognition and Inclusion, Proceedings of the International Symposium on Molecular Recognition and Inclusion*, 9th, Lyon, Sept. 7-12, 1996 (1998), Meeting Date 1996, 179-184. Publisher: Kluwer, Dordrecht, Neth

Abstract: A review with 23 refs. on topics of: metal-dependent induction of conformational chirality, propeller-like TPA derivs., a metal ion-differentiating fluorescent chemosensor, ternary complexes: mol. recognition and catalysis, and complexation.

Bibliographic Information

Fluorescent Cyclodextrins Responsive to Molecules and Metal Ions. Fluorescence Properties and Inclusion Phenomena of N α -Dansyl-L-lysine- β -cyclodextrin and Monensin-Incorporated N α -Dansyl-L-lysine- β -cyclodextrin. Ueno, Akihiko; Ikeda, Akira; Ikeda, Hiroshi; Ikeda, Tsukasa; Toda, Fujio. Department of Bioengineering Faculty of Bioscience and Biotechnology, Tokyo Institute of Technology, Midori-ku Yokohama, Japan. *Journal of Organic Chemistry* (1999), 64(2), 382-387.

Abstract: N α -Dansyl-L-lysine- β -cyclodextrin with a monensin unit (I; B = 6A-deoxy- β -cyclodextrin) was prepd. as a fluorescent chemosensor for mol. recognition. Its fluorescence properties and inclusion phenomena were examd. using N α -dansyl-L-lysine- β -cyclodextrin (II) and N ϵ -benzyloxycarbonyl-N α -dansyl-L-lysine- β -cyclodextrin (III) as ref. compds. The fluorescence peak intensities of these hosts are in the order II > I > III, suggesting that the dansyl unit of II is most deeply included in the β -cyclodextrin cavity. The host I exhibits two lifetimes, both in the absence of a guest [18.2 ns (81.8%) and 10.9 ns (18.2%)] and in the presence of 1-adamantanol (0.3 mM) [16.3 ns (17.8%) and 9.4 ns (82.2%)], demonstrating that I exists predominantly as a self-inclusion form with a longer lifetime and that it excludes the dansyl moiety to outside the cavity upon guest accommodation. A sodium cation in a soln. of I enhanced the binding ability of I and increased the guest-dependent fluorescence variation. All of these results demonstrate that the monensin moiety of I is effective in changing the environment around the cyclodextrin cavity by forming a ring-like conformation with a sodium ion in the center.



Bibliographic Information

Design of a new molecular fluorescent signalling system acting via both electron and energy transfer.

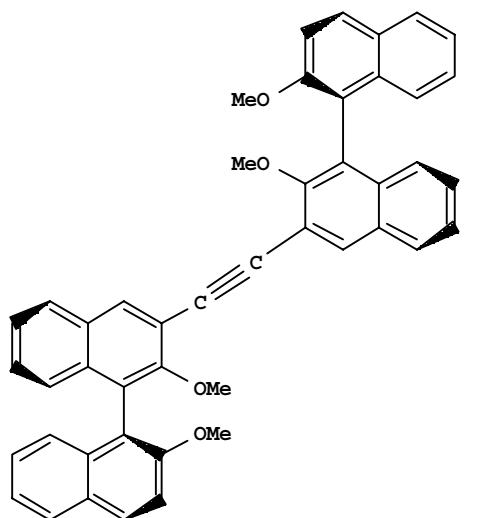
Wang, Pengfei; Wu, Shikang. Institute of Photographic Chemistry, The Chinese Academy of Sciences, Beijing, Peop. Rep. China. *Journal of Photochemistry and Photobiology, A: Chemistry* (1998), 118(1), 7-9. CODEN: JPPCEJ ISSN: 1010-6030. Journal written in English.

Abstract: A new mol. fluorescent signalling compd. has been designed and synthesized in this work. In a mol., there are two non-conjugated chromophores included, one of them acts as an electronic acceptor and energy transfer donor, while the other is used as an acceptor of energy transfer. The advantages of this design are as follows: first, it can lead to a long-wavelength emission upon excitation at a short wavelength after the system was protonated. The second is that this system offers a large flexibility in choosing dyes with different wavelength of absorption and emission.

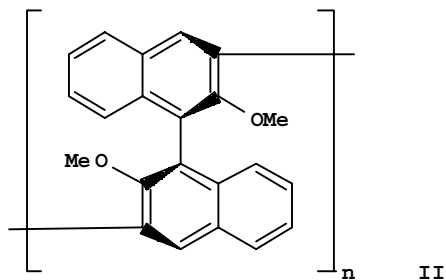
Bibliographic Information

Enantiomeric discrimination of chiral amines with new fluorescent chemosensors. Wang, Dong; Liu, Tian-Jun; Zhang, Wen-Chun; Zhang, Wen-Chun; Slaven, William T., IV; Li, Chao-Jun. Institute of Chemistry, Chinese Acad. Sci., Beijing, Peop. Rep. China. *Chemical Communications (Cambridge)* (1998), (16), 1747-1748.

Abstract: Fluorescent chiral sensors for the enantiomeric recognition of chiral amines were developed based on host-guest interaction. The chiral hosts used are dimeric (I) and oligomeric (II) binaphthol derivs. The chiral guest amines are D/L- α -phenylethylamines as well as D/L-phenylalanine Me esters.



I



II

Bibliographic Information

A squaraine-based sodium selective fluorescent chemosensor. Oguz, Umut; Akkaya, Engin U. Department of Chemistry, Middle East Technical University, Ankara, Turk. *Tetrahedron Letters* (1998), 39(32), 5857-5860.

Abstract: A novel squaraine with a lariat-crown ether cation-receptor unit was synthesized and shown to selectively respond to Na⁺ ions in polar protic solvents. The selectivity of the novel ligand, together with the impressive spectroscopic properties of squaraines yields a promising chemosensor.

Bibliographic Information

A fluorescent sensor for magnesium ions. Prodi, Luca; Bolletta, Fabrizio; Montalti, Marco;

Zaccheroni, Nelsi; Savage, Paul B.; Bradshaw, Jerald S.; Izatt, Reed M. Dipartimento di Chimica "G. Ciamician", Universita di Bologna, Italy. *Tetrahedron Letters* (1998), 39(31), 5451-5454.

Abstract: Diaza-18-crown-6 appended with two 5-chloro-8-hydroxyquinoline groups can serve as an effective chemosensor for Mg²⁺. The modified macrocycle will fluoresce in the presence of Mg²⁺ but not with other alk. earth ions at pH 7.2. Mg²⁺ concns. can be measured in the presence of Na²⁺, K⁺, Ca²⁺, Sr²⁺ and Ba²⁺.

Bibliographic Information

A new family of luminescent sensors for alkaline earth metal ions. Prodi, Luca; Bolletta, Fabrizio; Zaccheroni, Nelsi; Watt, C. Ian F.; Mooney, Nichola J. Dipartimento di Chimica G. Ciamician, Universita degli studi di Bologna, Bologna, Italy. *Chemistry--A European Journal* (1998), 4(6), 1090-1094.

Abstract: The effects on the photophys. properties of three crown ethers contg. the 1,8-dioxyxanthone residue caused by the complexation with Ba²⁺, Sr²⁺, and Ca²⁺ metal ions are reported. The strong enhancement of the fluorescence, the appearance of a long-lived delayed fluorescence, and a good selectivity towards Ba²⁺ ions prove that one of the reagent is an efficient fluorescent chemosensor for this ion. The range of selectivities shown by this family of crown ethers towards the alk. earth metal ions together with their favorable photophys. properties, make them suitable for the construction of (multi)sensory devices. The differences in the photophys. properties between the uncomplexed and complexed crown ethers can be accounted for by the stabilization of a different ground state conformer of the dioxyxanthone moiety by the metal ion within the cavity of the crown ether.

Bibliographic Information

Fluorescent functional recognition sites through molecular imprinting. A polymer-based fluorescent chemosensor for aqueous cAMP. [Erratum to document cited in CA129:14153]. Turkewitsch, Petra; Wandelt, Barbara; Darling, Graham D.; Powell, William S. Meakins-Christie Laboratories and the Montreal Chemist Institute Research Center Department of Medicine, McGill University, Montreal, QC, Can. *Analytical Chemistry* (1998), 70(13), 2771.

Abstract: The two Me groups of the fluorescent dye 1 in Scheme 1 (p 2026) were incorrectly represented as "CH₂" instead of "CH₃".

Bibliographic Information

Porous Shape Persistent Fluorescent Polymer Films: An Approach to TNT Sensory Materials. Yang, Jye-Shane; Swager, Timothy M. Department of Chemistry, Massachusetts Institution of Technology, Cambridge, MA, USA. *Journal of the American Chemical Society* (1998), 120(21), 5321-5322.

Abstract: Spin-cast films of a pentiptycene-derived phenyleneethynylene polymer, 2, display a fast fluorescence response (seconds) to vapors of 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), and 1,4-benzoquinone (BQ). The fluorescence attenuation of 2 is dependent on the time of exposure to these quenchers and on the thickness of thin films. Thinner films show a better response to TNT and DNT but the opposite is true for BQ. Such differences are attributed to different polymer-analyte interactions. For comparison, corresponding studies on an alkoxy-substituted phenyleneethynylene polymer, 3, were also carried out. The results indicate that 2 is superior to 3 as a fluorescent chemosensor in terms of sensitivity, selectivity, solvent soly. and solvent stability.

Bibliographic Information

Fluorescent Functional Recognition Sites through Molecular Imprinting. A Polymer-Based Fluorescent Chemosensor for Aqueous cAMP. Turkewitsch, Petra; Wandelt, Barbara; Darling, Graham D.; Powell, William S. Meakins-Christie Laboratories and the Montreal Chest Institute Research Center Department of Medicine, McGill University, Montreal, QC, Can. *Analytical Chemistry* (1998), 70(10), 2025-2030.

Abstract: A novel design for template-selective recognition sites in polymers prep'd. by mol.

imprinting is reported. Mol. imprints were prepd. against cAMP that contain a fluorescent dye, trans-4-[p-(N,N-dimethylamino)styryl]-N-vinylbenzylpyridinium chloride, as an integral part of the recognition cavity, thus serving as both the recognition element and the measuring element for the fluorescence detection of cAMP in aq. media. This fluorescent molecularly imprinted polymer displays a quenching of fluorescence in the presence of aq. cAMP, whereas almost no effect is obsd. in the presence of the structurally similar mol., cGMP. The assocn. const. for the binding of cAMP to the imprinted polymer was detd. to be in the order of 10^5 M^{-1} . Such fluorescent molecularly imprinted polymers contg. selective sites for cAMP may find applications as fluorescent chemosensors for the aq. detection of this mol.

Bibliographic Information

Fluorescent chemosensors for Cu^{2+} ions: fast, selective, and highly sensitive. Kramer, Roland. Anorganisch-Chemisches Institut der Universitat, Munster, Germany. *Angewandte Chemie, International Edition* (1998), 37(6), 772-773.

Abstract: A review, with 9 refs., is given on copper (II) detn. by fluorescent chemosensor mols.

Bibliographic Information

Molecular design of a PET-based chemosensor for uronic acids and sialic acids utilizing a cooperative action of boronic acid and metal chelate. Yamamoto, Masashi; Takeuchi, Masayuki; Shinkai, Seiji. Department of Chemical Science & Technology, Faculty of Engineering, Kyushu University, Fukuoka, Japan. *Tetrahedron* (1998), 54(13), 3125-3140.

Abstract: To exploit new artificial receptors for detection of uronic acids and sialic acids in an aq. system a novel fluorescent chemosensor mol. bearing both o-aminomethylphenylboronic acid group for diol binding and 1,10-phenanthroline-Zn(II) chelate moiety for carboxylate binding has been synthesized. The saccharide-binding process can be conveniently monitored by a fluorescence change which occurs by the photoinduced electron-transfer (PET) mechanism through a unit integrated in this mol. Fluorescence measurements indicate that assocn. for commonly occurring monosaccharides is little affected by Zn(II) addn. whereas that for uronic acids or sialic acids is enhanced in the presence of Zn(II) owing to the two-points interaction. PH Dependence, stoichiometry of the complexes, and complexation modes have been examd. This artificial receptor shows substantial affinity toward uronic acids and sialic acids in aq. methanol soln.

Bibliographic Information

A chiroptically enhanced fluorescent chemosensor. Castagnetto, Jesus M.; Canary, James W. Dep. Chem., New York Univ., New York, NY, USA. *Chemical Communications (Cambridge)* (1998), (2), 203-204.

Abstract: One sensor mol. gives both fluorescence and exciton-coupled CD signals upon metal ion complexation, suggesting a novel strategy for detection, identification and quantification of multiple analytes.

Bibliographic Information

Selective fluorescent chemosensor for fructose. Luis, G. Pina; Granda, M.; Badia, R.; Diaz-Garcia, Marta Elena. Dep. Analytical Chem., Univ. La Habana, Havana, Cuba. *Analyst (Cambridge, United Kingdom)* (1998), 123(1), 155-158.

Abstract: A chemosensing system for the selective recognition of fructose based on a reverse photoinduced electron transfer process was developed. A fluorescent boronic acid, m-dansylaminophenylboronic acid, reacts with fructose to produce an electron transfer, which results in the fluorescence quenching of the dye. The addn. of the sugar shifted the pKa from 8.13 to 7.80. A possible sensing mechanism is proposed. The anal. figures detd. in a batch approach were detection limit $5 \times 10^{-6} \text{ M}$, repeatability of 1% at the $1 \times 10^{-4} \text{ M}$ fructose level and linear calibration up to $3 \times 10^{-4} \text{ M}$. A flow injection system was also examd. and after the exptl. conditions had been optimized a selectivity study showed that only galactose (at a 1:2 fructose to galactose molar ratio) gave a pos. deviation. Several food samples were analyzed by the proposed flow injection procedure and the results agreed with those obtained

using an enzymic kit for food anal.

Bibliographic Information

Chemosensing in deep red: a squaraine-based fluorescent chemosensor for pH. Isgor, Yasemin G.; Akkaya, Engin U. Department of Chemistry, Middle East Technical University, Ankara, Turk. *Tetrahedron Letters* (1997), 38(42), 7417-7420.

Abstract: The authors synthesized and spectrally characterized a squaraine-based fluorescent chemosensor for pH. This chemosensor unlike many others, works in 100% aq. solns., signaling the pH change from 10 to 7 by a 14-fold increase in the emission intensity at 651 nm, when excited at the isosbestic point (614 nm). The av. pKa for the ionizable groups is 8.8. The chemosensor with its molar absorptivity > 200,000 and the quantum yield of 0.2, yield an impressive intrinsic brightness value of 40,000.

Bibliographic Information

A fluorescent chemosensor with selectivity for Hg(II). Chelatoselectivity via ligand immobilization. Yoon, J.; Ohler, N. E.; Vance, D. H.; Aumiller, W. D.; Czarnik, A. W. Department of Chemistry, Ohio State University, Columbus, OH, USA. *NATO ASI Series, Series C: Mathematical and Physical Sciences* (1997), 492(Chemosensors of Ion and Molecule Recognition), 189-194.

Abstract: Geometric immobilization of polyamine ligands is expected to change their binding properties toward practical ion discrimination. Chemosensor 5 senses only two transition metal ions in water- Hg(II)(Kd $\leq 1 \mu\text{M}$) and Cu(II)(Kd $56 \mu\text{M}$)- which can be compared with bindings of a non-immobilized ref. compd. (9-(trpnmethyl)- anthracene) with Hg(II)(Kd $14 \mu\text{M}$) and Cu(II)(Kd $39 \mu\text{M}$). A related bridged cyclen deriv. showed no effect on fluorescence by any metal ion examd. Probably the rigid immobilization of polyamine ligands onto a fluorophore framework may be employed successfully in the creation of selective chemosensors.

Bibliographic Information

Fluorescent chemosensors which take profit from the metal-ligand interaction. Fabbrizzi, L.; Francese, G.; Licchelli, M.; Pallavicini, P.; Perotii, A.; Poggi, A.; Sacchi, D.; Taglietti, A. Dipartimento di Chimica Generale, University di Pavia, Pavia, Italy. *NATO ASI Series, Series C: Mathematical and Physical Sciences* (1997), 492(Chemosensors of Ion and Molecule Recognition), 75-90.

Abstract: A review, with 16 refs., is given on some of the principles that guide the design of fluorescent sensors for transition metals. Fluorescent sensors for genuine transition metal ions such as NiII and CuII can be built by linking to the appropriate fluorophore a chelating poly-aza subunit displaying selective coordinating tendencies. The metal center quenches the excited state of the proximate light-emitting fragment and the recognition is signaled through the consequent fluorescence quenching. The photophys. inactive ZnII cation typically revives the fluorescence of fluorosensors contg. a polyamine receptor. However, ZnII coordination may also enable an intramol. electron transfer process in a polyamine bearing a fluorescent subunit and an electron donor/acceptor fragment, inducing fluorescence quenching. Coordinative interactions to ZnII centers can be used for anion sensing: an anthracene based fluorosensor contg. two ZnII polyamine subunits selectively binds the imidazolate anion (including that of L-histidine). Recognition is signaled by the fluorescence quenching induced by an electron transfer process from the anion to the fluorophore.

Bibliographic Information

New fluorescent readouts for protein interactions, gene expression, and membrane potential. Tsien, Roger Y. Departments of Pharmacology and Chemistry, Howard Hughes Medical Institute University of California, San Diego, La Jolla, CA, USA. *NATO ASI Series, Series C: Mathematical and Physical Sciences* (1997), 492(Chemosensors of Ion and Molecule Recognition), 17-21.

Abstract: Fluorescent chemosensors have traditionally been synthesized by org. chemists to measure specific ions or mols. In the future, many fluorescent chemosensors will be generated by mol. biol. Mols. from both sources will be used to measure not just specific chem. species but biol. signals or processes such

as membrane potential, protein-protein interaction, proteolytic activity, and gene expression. Future challenges include the design of chemosensors for post-translational modifications such as protein phosphorylation and metabolic indexes such as redox and phosphorylation potentials.

Bibliographic Information

Peptidyl fluorescent chemosensor for divalent zinc. Imperiali, Barbara; Walkup, Grant K. (California Institute of Technology, USA). PCT Int. Appl. (1997), 35 pp. CODEN: PIXXD2 WO 9735182 A1 19970925 Designated States W: JP. Designated States RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE. Patent written in English. Application: WO 97-US4672 19970321. Priority: US 96-620151 19960322. CAN 127:302663 AN 1997:640824 CAPLUS (Copyright 2002 ACS)

Abstract: The present invention provides a selective fluorescent chemosensor, sensitive to nanomolar concns. of zinc (II) and selective for this ion over Na⁺, Mg²⁺, Co²⁺.

Bibliographic Information

Fluorescent Chemosensor for Organic Guests and Copper(II) Ion Based on

Dansyldiethylenetriamine-Modified β -Cyclodextrin. Corradini, Roberto; Dossena, Arnaldo; Galaverna, Gianni; Marchelli, Rosangela; Panagia, Anna; Sartor, Giorgio. Dipartimento di Chimica Organica e Industriale, University of Parma, Parma, Italy. Journal of Organic Chemistry (1997), 62(18), 6283-6289.

Abstract: A modified cyclodextrin contg. a dansyldiethylenetriamine metal-binding group (6-deoxy-6-N-(N'-dansyldiethylenetriamino)- β -cyclodextrin, CD-dien-DNS) was synthesized. The conformation of CD-dien-DNS was studied by 2D NMR (ROESY spectra) in D₂O, by CD, and by fluorescence. The results were compared with those previously obtained with the analogous 6-deoxy-6-N-(N'-dansylethylenediamine)- β -cyclodextrin (CD-en-DNS) and were consistent with the self-inclusion of the dansyl group within the macrocycle cavity. However, the orientation of the dansyl group for CD-dien-DNS was found to be equatorial, whereas for CD-en-DNS it was axial, suggesting a dependence of the orientation of the dansyl group upon the length of the linker. In the presence of lipophilic org. mols., CD-dien-DNS showed sensing properties similar to those obsd. for CD-en-DNS, suggesting a similar "in-out" movement of the dansyl group, due to competitive inclusion of the guest. Unlike CD-en-DNS, CD-dien-DNS was found to be a fluorescent chemosensor for copper(II) ion, with a linear response up to a 1:1 molar ratio, suggesting that a more flexible conformation of the linker and the presence of addnl. binding sites allow binding of the metal ion by the amine and sulfonamide groups. Good selectivity for Cu(II), when compared with Fe(II), Co(II), Ni(II), and Zn(II), was obsd. The the CD-dien-DNS copper complex was shown to behave as a chemosensor for bifunctional mols., such as amino acids. In fact, upon addn. of alanine, tryptophan, and thyroxine, the negligible fluorescence intensity of Cu(CD-dien-DNS) complex was "switched on", with a response dependent on the amino acid side chain.

Bibliographic Information

Squaraine-based red-fluorescent chemosensor for pH. Akkaya, Engin U.; Isgor, Yasemin G. Department Chemistry, Middle East Technical University, Ankara, Turk. Book of Abstracts, 214th ACS National Meeting, Las Vegas, NV, September 7-11 (1997), ORGN-007. Publisher: American Chemical Society, Washington, D. C

Abstract: Fluorescent chemosensors signalling the presence of target analytes in the red-end of the visible spectrum are highly desirable for a no. of reasons, including a much lower background signal. We have synthesized and spectrally characterized a squaraine-based fluorescent chemosensor for pH. This chemosensor unlike many others, work in 100% aq. solns., signalling the pH change from 10 to 7 by a 14-fold increase in the emission intensity at 651 nm, when excited at the isosbestic point of 614 nm. The av. pK_a for the ionizable groups is found to be 8.8. The chemosensor with its molar extinction coeff. > 200,000 and the quantum yield of 0.2, yield an intrinsic brightness value of 40,000; an impressive value compared all known chemosensors.

Bibliographic Information

A squaraine-based near IR fluorescent chemosensor for calcium. Akkaya, Engin U.; Turkyilmaz, Serhan. Dep. Chemistry, Middle East Technical Univ., Ankara, Turk. *Tetrahedron Letters* (1997), 38(25), 4513-4516. CODEN: TELEAY ISSN: 0040-4039. Journal written in English.

Abstract: A red to NIR emitting, highly Ca²⁺-specific fluorescent chemosensor was synthesized. In pH 7.2 aq. buffers, the chemosensor signals Ca²⁺ by a decrease in emission intensity, whereas large excess of Mg²⁺ ions have no effect on either the absorption or the emission spectrum. The chemosensor probably is the prototype of a new generation of laser-diode excitable fluorescent chemosensors for Ca.

Bibliographic Information

One-pot synthesis of a red-fluorescent chemosensor from an azacrown, phloroglucinol and squaric acid: a simple in-solution construction of a functional molecular device. Oguz, Umut; Akkaya, Engin U. Dep. Chemistry, Middle East Technical Univ., Ankara, Turk. *Tetrahedron Letters* (1997), 38(25), 4509-4512.

Abstract: A long-wavelength fluorescent, squaraine-based chemosensor was synthesized in one step from com. available precursors. The resulting squaraine deriv. absorbs maximally at 635 nm ($\epsilon = 260,000$), with an emission peak at 665 nm. This azacrown-appended squaraine can be used to detect alk. and alk. earth metal ions in millimolar concns. in acetonitrile.

Bibliographic Information

A fluorescent chemosensor signaling only Hg(II) and Cu(II) in water. Yoon, Juyoung; Ohler, Norman E.; Vance, David H.; Aumiller, Wade D.; Czarnik, Anthony W. Dep. Chem., Ohio State Univ., Columbus, OH, USA. *Tetrahedron Letters* (1997), 38(22), 3845-3848. CODEN: TELEAY ISSN: 0040-4039. Journal written in English.

Abstract: Geometric immobilization of polyamine ligands is expected to change their binding properties toward practical ion discrimination. Chemosensor 5 senses only 2 transition metal ions in water, Hg(II) ($K_d \leq 1 \mu\text{M}$) and Cu(II) ($K_d 56 \mu\text{M}$), which can be compared with binds of a non-immobilized ref. compd. 9-(trpnmethyl)-anthracene with Hg(II) ($K_d 14 \mu\text{M}$) and Cu(II) ($K_d 39 \mu\text{M}$). A related bridged cyclen deriv. showed no effect on fluorescence by any metal ion examd.

Bibliographic Information

A fluorescent chemosensor for the copper(II) ion. De Santis, Giancarlo; Fabbrizzi, Luigi; Licchelli, Maurizio; Mangano, Carlo; Sacchi, Donatella; Sardone, Nicola. Dipartimento di Scienze, Universita di G. D'Annunzio, viale Pindaro 42, I-65127, Pescara, Italy. *Inorganica Chimica Acta* (1997), 257(1), 69-76. CODEN: ICHAA3 ISSN: 0020-1693. Journal written in English.

Abstract: The two-component system anthracene-9-carboxylic acid 1,4,8,11-tetrathiacyclotetradecan-6-yl ester (1) was synthesized, structurally characterized and studied as a fluorescent chemosensor for the CuII ion. Crystallog. details for 1: space group P21/c with $a = 9.894(2)$, $b = 24.608(2)$, $c = 10.759(2)$.ANG., $\alpha = 90$, $\beta = 105.88$, $\gamma = 90^\circ$, $V = 2519.7$.ANG., $Z = 4$ ($R = 0.088$, $R_w = 0.066$). In EtOH soln. 1 selectively incorporates CuII into its tetrathia crown component in the presence of other 3d metal ions and signals the recognition through the quenching of the fluorescence of the anthracene fragment. Quenching of the photoexcited state (which has a charge transfer nature) takes place through a photo-induced electron transfer from the fluorophore to the metal center and involves the CuII/CuI couple. The d10 cation AgI competes successfully with CuII for the tetrathia cavity of 1 in an EtOH soln. (not in an MeCN soln.), but the occurrence of the metal/receptor interaction cannot be signaled, due to the poor redox activity of the nontransition cation AgI.

Bibliographic Information

Dansyl-modified cyclodextrins as fluorescent chemosensors for molecular recognition. Hamasaki, Keita; Usui, Shinji; Ikeda, Hiroshi; Ikeda, Tsukasa; Ueno, Akihiko. Faculty Bioscience Biotechnology, Tokyo Institute Technology, Yokohama, Japan. *Supramolecular Chemistry* (1997), 8(2), 125-135. CODEN: SCHEER ISSN: 1061-0278. Journal written in English.

Abstract: α -, β -, And γ -cyclodextrins (CDs) bearing a dansyl or dansylglycine moiety at the primary or secondary side of the CD were synthesized as fluorescent indicators for mol. recognition. The CDs with the moiety at the secondary OH group have an asym. cavity with a distorted CD framework because of the conversion of one glucose unit to an altrose residue. The effects of this distortion of the CD ring on the sensing abilities were examd. and compared with sym. CDs bearing the dansyl moiety at the primary side. The results demonstrate that the asym. CDs are unfavorable to accommodate the guest species due to the cavity narrowed by the distortion contrasting with the observation that the sym. CDs exhibit remarkable sensing abilities for various guests.

Bibliographic Information

A novel porphyrin based fluorescent chemosensor using a molecular recognition approach.

D'Souza, Francis; Deviprasad, Golapalli R.; Hsieh, Yi-Ying. Dep. Chem., Wichita State Univ., Wichita, KS, USA. Chemical Communications (Cambridge) (1997), (6), 533-534. CODEN: CHCOFS ISSN: 1359-7345. Journal written in English.

Abstract: Free-base porphyrin covalently linked to quinone exhibits enhanced fluorescence on coupling the quinone with hydroquinone, primarily due to the unfavorable conditions for an electron transfer reaction between the singlet excited porphyrin and the newly formed quinone-hydroquinone entity.

Bibliographic Information

A chiroptically enhanced fluorescent sensor. Castagnetto, Jesus M.; Canary, James W. Department Chemistry, New York University, New York, NY, USA. Book of Abstracts, 213th ACS National Meeting, San Francisco, April 13-17 (1997), BTEC-072. Publisher: American Chemical Society, Washington, D. C

Abstract: The ligand α -MeBQPA (L) acts as an intrinsic fluorescent chemosensor for diamagnetic ions such as ZnII and CdII, presenting enhanced fluorescence when bound to these metal ions. The ligand L also displays highly anisotropic absorption (CD spectra) when bound to ions such as ZnII or CuII. Together, the fluorescence and CD properties of the complexes allow L to report not only the presence of a metal ion, but also its identity.

Bibliographic Information

Design and synthesis of novel fluorescent chemosensors for biologically active molecules. Cooper, Martin E.; Hoag, Benjamin P.; Gin, Douglas L. Dep. Chem., Univ. California, Berkeley, CA, USA. Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) (1997), 38(1), 209-210.

Abstract: Cholesterol is linked to a fluorescent "reporter" mol. and imprinted into an ethyleneglycol dimethacrylate polymer network for specific detection of biol. active mols. A new, more sensitive fluorescent monomer was prepd. and polymd. into a network which is highly sensitive to proton donor mols. We intend to integrate this functional fluorescent mol. into an imprinted polymer format.

Bibliographic Information

Fluorescent Chemosensors for Divalent Zinc Based on Zinc Finger Domains. Enhanced Oxidative Stability, Metal Binding Affinity, and Structural and Functional Characterization. Walkup, Grant K.; Imperiali, Barbara. Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA. Journal of the American Chemical Society (1997), 119(15), 3443-3450.

Abstract: The design, synthesis, and characterization of a family of peptides modeled after the zinc finger domains, which has led to the prodn. of a fluorescent peptidyl sensor for divalent zinc with enhanced oxidative stability, are reported. The chemosensor design comprises a synthetic peptidyl template and a covalently attached fluorescent reporter which is sensitive to metal-induced conformational changes in the polypeptide construct. The modular synthetic approach employed for the construction of these chemosensors allows independent modification of the metal coordination sphere and the fluorescent reporter group. The structural, fluorescence, and zinc binding properties of these peptides and the effects of integrating various environment sensitive fluorophores, 4-(dimethylamino)benzamide, 5-

(dimethylamino)naphthalenesulfonamide, and 3-carboxamidocoumarin, are described. Manipulation of the ligand sphere, by removal of one of the pair of thiolate ligands, was undertaken to enhance the oxidative stability of the chemosensor. For each of these peptides, the apparent dissociation constant of the peptide-zinc complex has been determined by spectroscopic methods. High-affinity binding, with dissociation constants ranging from 7 pM to 65 nM, is observed.

Bibliographic Information

Peptide platforms for metal cation sensing. Imperiali, Barbara. Division Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA. Book of Abstracts, 213th ACS National Meeting, San Francisco, April 13-17 (1997), ORGN-473. Publisher: American Chemical Society, Washington, D. C.

Abstract: Recent efforts have been directed toward the production of fluorescent chemosensors for trace quantities of divalent transition metal cations. Chemosensors for divalent metals require two components to function - a metal ion recognition and binding unit and a signaling mechanism. For example, to effect highly selective binding to divalent zinc ions, a chemically synthesized peptide patterned after the zinc finger peptides has been employed. To this template, fluorophores that have solvent-dependent emission properties have been attached. Upon binding zinc, the peptide folds and the change in environment experienced by the pendant fluorophore is detected by fluorescence spectroscopy. A fluorescent chemosensor for divalent zinc sensitive to nanomolar concentrations of divalent zinc has been prepared. This chemosensor allows sensitive measurements of free zinc ion to be made but is oxidatively labile; recent efforts to address this problem will be presented. In addition, a peptide-based chemosensors with selectivities for other transition metal ions will be introduced.

Bibliographic Information

Nanoparticles imprinted with recognition sites for target molecules. Darling, Graham D.; Heisler, Seymour; Stranix, Brent R.; Turkewitsch, Petra; Wandelt, Barbara. (Research Corporation Technologies, Inc., USA). PCT Int. Appl. (1996), 71 pp. CODEN: PIXXD2 WO 9641173 A1 19961219 Designated States W: CA, JP. Designated States RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE. Patent written in English. Application: WO 96-US7936 19960529. Priority: US 95-473240 19950607. CAN 126:152242 AN 1997:140282 CAPLUS (Copyright 2002 ACS)

Abstract: The present invention provides solid imprinted particles comprising recognition sites spaced on the surface thereof which selectively bind a preselected template compound (T), wherein said recognition sites are each defined by a shaped polymeric matrix conforming to the shape and size of T, comprising a unit of the formula -B-Det, wherein B is bound to the polymeric matrix and also comprises a functional group which reversibly binds to T, and Det is a moiety capable of generating a detectable signal which changes following binding of B to template compound T.

Bibliographic Information

A squaraine-based long wavelength fluorescent chemosensor for calcium. Akkaya, E. U. Department Chemistry, Middle East Technical University, Ankara, Turk. Book of Abstracts, 212th ACS National Meeting, Orlando, FL, August 25-29 (1996), ORGN-137. Publisher: American Chemical Society, Washington, D. C.

Abstract: We have synthesized a fluorescent chemosensor that signals Ca²⁺ concentration both by a hypochromic change in the absorption spectrum and a decrease in the fluorescence intensity. The chemosensor is designed to have two highly Calcium selective BAPTA chelator units linked by a squaraine moiety, thus forming a fluorescent squaraine system which is extremely sensitive to Ca²⁺ concentrations in the micromolar range. The signal results from a de-conjugation of donor alkyl-amino functions on Ca²⁺ chelation, decreasing molar extinction coefficient from 300,000 to 90,000. However, the most interesting attribute of this chemosensor is its very long wavelength absorption (690 nm) and emission peaks (725 nm). Such long excitation and emission wavelengths of this chemosensor would yield a fluorescence signal which is essentially free of native fluorescence, when applied in vivo.

Bibliographic Information

Chemical communication using fluorescent chemosensors. Czarnik, Anthony W. Department of Chemistry, Ohio State University, Columbus, OH, USA. *Trends in Organic Chemistry* (1993), 4(1), 123-138.

Abstract: A review, with 39 refs. Large chelation-enhanced fluorescence (CHEF) effects upon the binding of metal ions, phosphates, and carboxylates to conjugate probes, providing large, readily measurable signals to these mol. recognition events were previously described. In understanding the structural requirements for CHEF, it is now possible to use the vast body of information on selective binding by azacrowns and cryptands in the synthesis of selective fluorescence probes. For example, a conjugate probe that allows for the selective, simultaneous assay of Zn(II) and Cd(II) ions was synthesized and will be described. In the homologous series of anthrylazamacrocycles that demonstrate chelation-enhanced fluorescence (CHEF) upon Zn(II) or Cd(II) binding in water, the pentacyclen deriv. uniquely complexes Cd(II) with perturbation of the emission spectrum. The binding of anions such as phosphate and citrate give rise to fluorescence enhancements as large as 6-fold; an obsd. pH dependence on the magnitude of fluorescence enhancements upon phosphate binding points to intracomplex protonation of the benzylic nitrogen by the HPO₄²⁻ ion as the origin of this CHEF effect. Anthrylpolyamine conjugate probes yield large (up to 80-fold) changes in fluorescence upon binding to biol. polyanions (e.g., DNA, heparin, and polyglutamate) at μM concns. These fluorescence changes were used as the basis for a fluorometric assay of heparinase activity.

Bibliographic Information

Design and Evaluation of a Peptidyl Fluorescent Chemosensor for Divalent Zinc. Walkup, Grant K.; Imperiali, Barbara. Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA. *J. Am. Chem. Soc.* (1996), 118(12), 3053-4. CODEN: JACSAT ISSN: 0002-7863. Journal written in English.

Abstract: The design, synthesis, and characterization of a highly selective peptidyl fluorescent chemosensor for Zn²⁺ is presented. This chemosensor comprises a synthetic peptidyl template based upon a Zn finger domain, and a covalently attached fluorescent reporter which is sensitive to metal-induced conformational changes in the polypeptide construct. This approach combines the sensitivity of fluorescence detection with the remarkable cation selectivity of the Zn fingers. The Zn sensor, ZNS1, is capable of detecting nanomolar concns. of Zn²⁺ in the presence of 50 mM Mg²⁺ and 100 μM Co²⁺, demonstrating the potential of this approach in environmental and biomedical applications. A modular synthetic approach was developed, which allows independent modification of the metal coordination sphere and the fluorophore for future construction of sensors for other metal cations.

Bibliographic Information

Fluorescent Chemosensors Based on Energy Migration in Conjugated Polymers: The Molecular Wire Approach to Increased Sensitivity. Zhou, Qin; Swager, Timothy M. Department of Chemistry, University of Pennsylvania, Philadelphia, PA, USA. *J. Am. Chem. Soc.* (1995), 117(50), 12593-602.

Abstract: The authors demonstrate herein how conjugated polymers (mol. wires) can be used to interconnect (wire in series) receptors to produce fluorescent chemosensory systems with sensitivity enhancements over single receptor analogs. The enhancement mechanism in the polyreceptor materials is based on an energy migration scheme in which excitations, diffuse along the polymer backbone. Analyte binding produces trapping sites for the excitations which results in greatly attenuated emission intensity. Three different cyclophane-based receptor systems that bind paraquat were studied. These systems are quenched by paraquat binding, and the quenching enhancements relative to a monomeric model compd. were used to det. the efficiency of energy migration. Two polymers with related poly(phenyleneethynylene) structures were studied, and the all-para system was found to exhibit more facile energy migration than the more electronically localized analog that contained meta linkages. The para polyreceptor system was found to display a 65-fold enhancement in sensitivity to paraquat as compared to a model monoreceptor fluorescent chemosensor. However, delocalization alone is not sufficient to produce facile energy migration, and the more delocalized polythiophenes appear to be less effective at energy migration than the para poly(phenyleneethynylene) material. Paraquat-induced fluorescent quenching studies on homologous polymers that lacked the cyclophane receptors were also

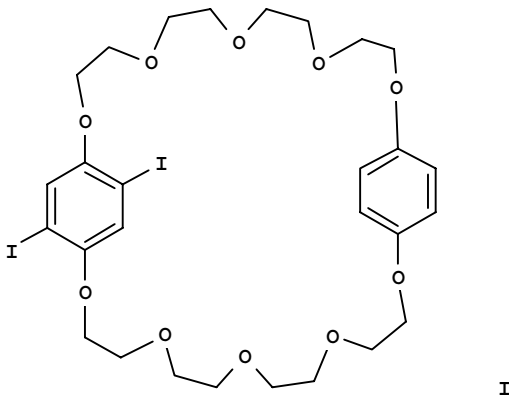
performed. Diffusive quenching by paraquat is enhanced by energy migration.

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A conjugated pseudopolyrotaxane: Demonstration of a highly sensitive fluorescent chemosensor.

Zhou, Qin; Ezer, Mayer R.; Swager, Timothy M. Department Chemistry, University Pennsylvania, Philadelphia, PA, USA. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) (1995), 36(1), 607-8.

Abstract: I is polymd. with 2,5-diethynyl-1,4-(N,N-dioctyl)benzenedicarboxamide to give fluorescent chemosensors, based on an electron transfer quenching mechanism. A model compd. is prepd. by reaction of I with p-dodecyloxyphenyleneacetylene. The quenching ability of the sensors and model compd. are discussed with respect to fluorophore vs. paraquat concn.

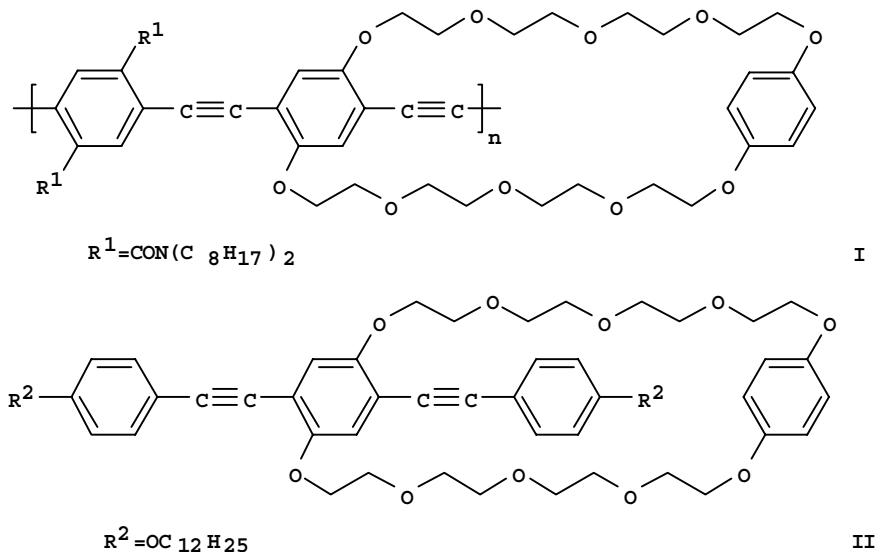


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Method for enhancing the sensitivity of fluorescent chemosensors: energy migration in conjugated

polymers. Zhou, Qin; Swager, Timothy M. Department of Chemistry, University of Pennsylvania, Philadelphia, PA, USA. J. Am. Chem. Soc. (1995), 117(26), 7017-18. CODEN: JACSAT ISSN: 0002-7863. Journal written in English.

Abstract: A new method for the enhancement of a fluorescent chemosensory response using conjugated polymers is reported. This method makes use of the delocalized electronic structure of these materials which allows the excited state to migrate to an occupied receptor site. In the conjugated polymer I each repeating unit displays a cyclophane receptor which binds paraquat ($K_a \approx 1600 \text{ M}^{-1}$). The binding of paraquat to I and II results in electron transfer quenching. The relative amt. of quenching in I is enhanced relative to II due to energy migration to the occupied sites. Theor., I can exhibit a max. sensitivity which is n times greater than II where n is the d.p. This effect leads to an enhancement in the static quenching consts. as detd. by the Stern-Volmer relation from 1600 M^{-1} for I to $105,000 \text{ M}^{-1}$ for II ($M_n = 122,500$). Polymers lacking receptor groups also displayed enhanced dynamic quenching consts. relative to monomeric analogs.



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Fluorescent chemosensors for cations, anions, and neutral analytes. Czarnik, Anthony W. Department of Chemistry, Ohio State University, Columbus, OH, USA. *Top. Fluoresc. Spectrosc.* (1994), 4 49-70.

Abstract: A review, with 26 refs., is given on the detn. of cations, anions, and neutral analytes using fluorescent substances, esp. chelating agents.

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Coumarinic fluorescent chemosensors for the detection of transition metal ions. Bourson, J.; Badaoui, F.; Valeur, B. Laboratoire de Chimie Generale, CNRS ER77, Paris, Fr. *J. Fluoresc.* (1994), 4(4), 275-7.

Abstract: Fluoroionophores consisting of coumarin-153 linked to mono- and diaza-crown ethers are able to complex transition metal cations (Ni^{2+} , Zn^{2+} , Cd^{2+}) and Pb^{2+} , with concomitant large changes in photophys. properties. The stability consts. in MeCN are $>3 \times 10^6 \text{ M}^{-1}$ except for Ni^{2+} .

Bibliographic Information

Fluorescent chemosensors of ion and molecule recognition. Recent applications to pyrophosphate and to dopamine sensing. Czarnik, Anthony W. Department Chemistry, Ohio State University, Columbus, OH, USA. *ACS Symp. Ser.* (1994), 561(INTERFACIAL DESIGN AND CHEMICAL SENSING), 314-23.

Abstract: A review, with 17 refs., is given. 1,8-Bis(TRPN)methylanthracene, available from 1,8-dibromomethylanthracene, binds phosphate and pyrophosphate anions in aq. soln., pH 7, with signalling in the form of chelation enhanced fluorescence. The affinity of this convergent chemosensor for pyrophosphate ($K_d = 2.9 \mu\text{M}$) is over 2000-times that for phosphate ($K_d = 6.3 \text{ mM}$); a ref. nonconvergent chemosensor [1-mono(TRPN)methylanthracene] displays only a 100-fold difference in binding affinities. The ion discrimination thus realized permits real-time anal. in the hydrolysis of pyrophosphate by inorg. pyrophosphatase. It was known for almost 35 yr that catechol complexes reversibly to boronic acids. 2-Anthrylboronic acid complexes catechol in H_2O with $K_d 330 \mu\text{M}$ and concomitant 20-fold redn. in fluorescence intensity. L-DOPA and dopamine behave similarly, suggesting a mechanism for the development of real-time sensing schemes.

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Real-Time Assay of Inorganic Pyrophosphatase Using a High-Affinity Chelation-Enhanced Fluorescence Chemosensor. Vance, David H.; Czarnik, Anthony W. Department of Chemistry, Ohio State University, Columbus, OH, USA. *J. Am. Chem. Soc.* (1994), 116(20), 9397-8.

Abstract: The spectroscopic signaling of nonquenching inorg. anions at submillimolar concns. has not been described heretofore. In this paper, the authors report the synthesis of a convergently functionalized fluorescent chemosensor possessing a binding region of appropriate dimensions to chelate the pyrophosphate ion. 1,8-Bis(TRPNmethyl)anthracene, available from 1,8-di(bromomethyl)anthracene, binds phosphate and pyrophosphate anions in aq. soln., pH 7, with signaling in the form of chelation enhanced fluorescence. The affinity of this convergent chemosensor for pyrophosphate ($K_d = 2.9 \mu\text{M}$) is over 2000-times that for phosphate ($K_d = 6.3 \text{ mM}$); a ref. nonconvergent chemosensor [1-(TRPNmethyl)anthracene] displays only a 100-fold difference in binding affinities. The ion discrimination thus realized permits real-time anal. in the hydrolysis of pyrophosphate by inorg. pyrophosphatase.

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Chemical Communication in Water Using Fluorescent Chemosensors. Czarnik, Anthony W. Department of Chemistry, Ohio State University, Columbus, OH, USA. *Acc. Chem. Res.* (1994), 27(10), 302-8.

Abstract: A review with 29 refs. summarizing advances, mostly by the author's group, in the design of conjugate chemosensors, esp. as applied to their use in aq. soln. Topics covered include: metal ion sensing, anion sensing, polymeric anion sensing (e.g., DNA, heparin), and neutral ion sensing.

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Chemical communication of enzymic ATP hydrolysis using a fluorescent chemosensor. Van Arman, Scott A.; Czarnik, Anthony W. Dep. Chem., Ohio State Univ., Columbus, OH, USA. *Supramol. Chem.* (1993), 1(2), 99-101.

Abstract: An anthrylpolyamine chemosensor, whose fluorescence is partially quenched upon electrostatic complexation to ATP, can be used to monitor the action of an enzyme (apyrase) that hydrolyzes ATP to AMP and inorg. phosphate.

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Fluorescent chemosensors for metal and non-metal ions in aqueous solution based on the CHEF paradigm. Czarnik, Anthony W. Dep. Chem., Ohio State Univ., Columbus, OH, USA. *Adv. Supramol. Chem.* (1993), 3 131-57.

Abstract: A review, with 25 refs., is given on chelation enhanced fluorescence (CHEF) in 9,10-bis(TMEDA)anthracene, chelation enhanced fluorescence of anthrylazamacrocyclic chemosensors in aq. soln., chelatoselective fluorescence perturbation in an anthrylazamacrocyclic CHEF sensor, chelation enhanced fluorescence detection of non-metal ions, and an assay for enzyme-catalyzed polyanion hydrolysis based on template-directed excimer formation.

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Fluorescent chemosensors for monitoring potassium in blood and across biological membranes. Masilamani, Divakar; Lucas, Mariann E. Biotechnol. Dep., Allied-Signal Inc., Morristown, NJ, USA. *ACS Symp. Ser.* (1993), 538(Fluorescent Chemosensors for Ion and Molecule Recognition), 162-82.

Abstract: A rational approach to develop a fluorescent chemosensor for potassium is presented.

Bibliographic Information

Supramolecular chemistry, fluorescence, and sensing. Czarnik, Anthony W. Dep. Chem., Ohio State Univ., Columbus, OH, USA. *ACS Symp. Ser.* (1993), 538(Fluorescent Chemosensors for Ion and Molecule Recognition), 1-9.

Abstract: A discussion, with 22 refs., is given on supramol. chem., fluorescence, and sensing as an introduction to a symposium with the theme: synthesis of abiotic mols. that sense analyte concns. with fluorescent signal transduction: fluorescent chemosensors. Section headings include: binding a mol. entity with selectivity, a brief introduction to fluorescence, fluorescence as a signal transduction mechanism, chem. mechanisms for fluorescence modulation, lifetime measurement, and what mechanisms for binding and signal transduction intersect.

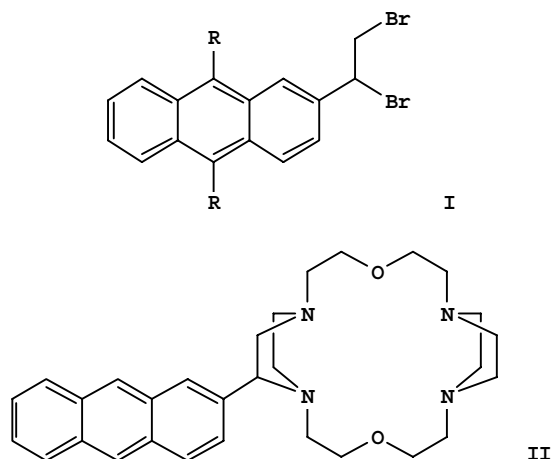
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Fluorescent Chemosensors for Ion and Molecule Recognition. (Developed from a Symposium Sponsored by the Division of Organic Chemistry at the 204th National Meeting of the American Chemical Society, Washington, DC, August 23-28, 1992.) [In: ACS Symp. Ser., 1993; 538]. Czarnik, Anthony W.; Editor. USA. (1993), 235 pp. Publisher: (ACS, Washington, D. C.) Book written in English.

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New reagents for the syntheses of fluorescent chemosensors. Anthrylogous ethylene dibromides. Chae, Mi Young; Cherian, Xavier M.; Czarnik, Anthony W. Dep. Chem., Ohio State Univ., Columbus, OH, USA. J. Org. Chem. (1993), 58(21), 5797-801.

Abstract: Two new 2-(1,2-dibromoethyl)anthracenes I (R = H, Me) were prepd. that serve as anthrylogous derivs. of ethylene dibromide, an important building block used in the construction of crown ethers, aza macrocycles, and cryptands. I (R = H) was utilized in the syntheses of fluorescent chemosensor II retaining the essential binding properties of the parent ligands.



Bibliographic Information

Fluorescent sensors of molecular recognition. Modified cyclodextrins capable of exhibiting guest-responsive twisted intramolecular charge transfer fluorescence. Hamasaki, Keita; Ikeda, Hiroshi; Nakamura, Asao; Ueno, Akihiko; Toda, Fujio; Suzuki, Iwao; Osa, Tetsuo. Fac. Biosci. Biotechnol., Tokyo Inst. Technol., Yokohama, Japan. J. Am. Chem. Soc. (1993), 115(12), 5035-40.

Abstract: P-(dimethylamino)benzoyl (DMAB) derivs. of α -, β -, and γ -cyclodextrin (DMAB- α CyD, DMAB- β CyD, and DMAB- γ CyD, resp.) have been synthesized as fluorescent sensors of mol. recognition. These compds. show dual fluorescence emission arising from normal planar (NP) and twisted intramolecular charge transfer (TICT) excited states, and among them strong TICT emission was obsd. for DMAB- β CyD. The induced CD spectra of the derivs. suggest that only DMAB- β CyD among other derivs. binds the DMAB moiety into its own cavity, forming an intramol. inclusion complex. This conformation was confirmed by the anal. of its ¹H-NMR data and was related to its strong TICT emission. The intensity of

the TICT emission of DMAB- β CyD decreased markedly with increasing concn. of cyclic alcs., monoterpenes, or steroids. This observation was explained by the guest-induced location change of the DMAB moiety from inside to outside the cavity. Since the TICT emission intensity depended on the size, shape, and polarity of the guest mols., DMAB- β CyD was useful as a fluorescent chemosensor of mol. recognition.

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Fluorescent chemosensors of carbohydrates. A means of chemically communicating the binding of polyols in water based on chelation-enhanced quenching. Yoon, Juyoung; Czarnik, Anthony W.. Dep. Chem., Ohio State Univ., Columbus, OH, USA. J. Am. Chem. Soc. (1992), 114(14), 5874-5.

Abstract: 2-Anthrylboronic acid (I; pKa 8.8) displays decreased fluorescence in the boronate form compared with its boronic acid form, which is attributed to photoinduced electron transfer. When I complexes to polyols such as fructose, the pKa of the complex decreases; thus, the fluorimetrically detd. pKa of the I:fructose borate ester is 5.9. These properties combined permit polyol complexation in water to be obsd. spectrofluorimetrically, which has not been reported previously. Fructose binds with a fluorimetrically detd. Kd of 3.7 mM.

