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A pyrene-functionalized triazole-linked hexahomotrioxacalix[3]arene as a fluorescent chemosensor for Zn^{2+} ions

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ABSTRACT

A new pyrenyl appended hexahomotrioxacalix[3]arene **L** featuring 1,2,3-triazole linkers was synthesized as a fluorescent chemosensor for Zn^{2+} in mixed aqueous media. It exhibited high affinity toward Zn^{2+}, and the monomer and excimer emission of the pyrene moieties could be adjusted. The binding stoichiometry of the $\mathbf{L}\cdot Zn^{2+}$ complex was determined to be 1:1, and the association constant (Ka) was found to be $7.05 \times 10^4\ M^{-1}$. The binding behavior with Zn^{2+} has been confirmed by ^1H NMR spectroscopic analysis.

1. Introduction

The development of new chemosensors for the efficient detection of heavy and transition metal (HTM) ions is currently a task of prime importance for medical, environmental and biological applications [1,2]. Among different types of chemosensors, fluorescent chemosensors generally offer distinct advantages in terms of sensitivity, selectivity and response time. Thus the design and synthesis of new fluorescent chemosensors for the selective recognition of the HTM ions have attracted considerable interest in recent years [3,4].

Fluorescent chemosensors normally consist of an ion recognition unit (ionophore) and a fluorogenic unit (fluorophore). An effective fluorescence chemosensor must convert the event of recognition by the ionophore into an easily monitored and highly sensitive fluorescence signal [5]. As fluorogenic units, photoactive pyrenyl substituents are very attractive due to their long fluorescence lifetime, pure blue fluorescence, strong and well characterized emissions and chemical stabilities [6]. In particular, the monomer and excimer emissions are observed at considerably different wavelengths depending on the relative proximity of the pyrene moieties [7].

Calixarenes have been extensively used as molecular platforms for the design and construction of different kinds of excellent receptors in molecular recognition by easy chemical modifications. As a new generation of calixarenes, hexahomotrioxacalix[3]arenes are related to both calixarenes and crown ethers, and possess a three-dimensional cavity with a C_3 symmetric structure. They exhibit characteristic affinities for metal cations [8,9], ammonium cations [10,11], and fullerene derivatives [12,13]. In other words, use of the hexahomotrioxacalix[3]arene as the platform has potential application in the development of novel fluorescence chemosensors.

The Cu(I)-catalyzed 1,3-dipolar cycloaddition of alkynes and azides ('Click' reaction) has provided a straightforward molecular linking strategy adopted in a wide range of synthetic applications [14–17]. The resulting 1,2,3-triazole group served not only as an efficient covalent linker, but also a binding site for specific metal cations and anions. On the basis of the wonderful complexation between triazole and metal cations, a number of triazole-based fluorescent chemosensors have been reported [18–20]. However, to date, triazole has been scarcely exploited for the functionalization of the hexahomotrioxacalix[3]arene scaffold.

Taking advantage of the easily-synthesized triazole binding site and the excellent fluorescent properties of pyrene, it prompted us to explore the possibility of introducing the pyrene at the hexahomotrioxacalix[3]arene for metal cation recognition. In the present manuscript, we reported the synthesis and fluorometric properties of pyrenyl appended hexahomotrioxacalix[3]arene **L** which was

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found to exhibit high selectivity toward Zn^{2+} in mixed aqueous media.

2. Experimental

2.1. General

Unless otherwise stated, all reagents used were purchased from commercial sources and were used without further purification. All the solvents used were dried and distilled by the usual procedures before use. All melting points were determined using a Yanagimoto MP-S1. ^1H NMR and ^{13}C NMR spectra were recorded on a Nippon Denshi JEOL FT-300 NMR spectrometer and a Varian-400MRvnmrs400 with $SiMe_4$ as an internal reference: *J*-values are given in Hz. IR spectra were measured as KBr pellets or as liquid films on NaCl plates in a Nippon Denshi JIR-AQ2OM spectrophotometer. UV spectra were measured by a Shimadzu UV-3150UV-vis-NIR spectrophotometer. Fluorescence spectroscopic studies of compounds in solution were performed in a semi-micro fluorescence cell (Hellma®, 104F-QS, 10 × 4 mm, 1400 μL) with a Varian Cary Eclipse spectrophotometer. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 mass spectrometer at an ionization energy of 70 eV using a direct inlet system through GLC. Elemental analyses were performed by a Yanaco MT-5.

2.2. Synthesis

Compounds **1** [21], **2** [22] and **3** [23] were prepared following the reported procedures.

2.2.1. General procedure for synthesis of compound **L**

Copper iodide (10 mg) was added to compound **1** (200 mg, 0.27 mmol) and 1-azidomethylpyrene (230 mg, 0.89 mmol) in a 30 mL mixture of THF/H_2O (5:1, v/v) and the mixture was heated at 70 °C for 24 h. The resulting solution was cooled and extracted twice with chloroform. The chloroform layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue obtained was purified using a silica gel column eluting with 1:1 hexane/chloroform to give the desired material **L** (295 mg, 72%) as a white solid. m.p. 214–216 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.27–1.31 (t, 9H, $COOCH_2CH_3$, *J* = 6.8 Hz), 4.17–4.20 (d, 6H, Ar$CH_2(eq)$O, *J* = 13.2 Hz), 4.19–4.24 (q, 6H, $COOCH_2CH_3$, *J* = 6.8 Hz), 4.31 (s, 6H, ArO—CH_2–triazole), 4.31–4.34 (d, 6H, Ar$CH_2(ax)$O, *J* = 13.2 Hz), 5.78 (s, 6H, triazole–CH_2–pyrene), 7.29 (s, 3H, triazole–*H*), 7.39 (s, 6H, Ar*H*), 7.64–7.66 (d, 3H, pyrene–*H*, *J* = 8.0 Hz), 7.80–7.88 (m, 12H, pyrene–*H*), 7.90–7.94 (t, 6H, pyrene–*H*, *J* = 8.0 Hz), 7.98–8.00 (d, 3H, pyrene–*H*, *J* = 8.0 Hz), 8.02–8.04 (d, 3H, pyrene–*H*, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.26, 51.84, 60.56, 66.94, 68.86, 121.73, 123.40, 124.67, 125.48, 125.59, 126.06, 126.13, 126.90, 127.04, 127.27, 127.94, 128.64, 128.72, 130.80, 131.06, 131.66, 131.78, 143.59, 158.23, 165.40. FABMS: *m*/*z* 1510.56 (M^+), 1511.57($M+H^+$). Anal. calcd for $C_{93}H_{75}N_9O_{12}$ (1510.64): C 73.94, H 5.00, N 8.34. found: C 73.89, H 5.04, N 8.36.

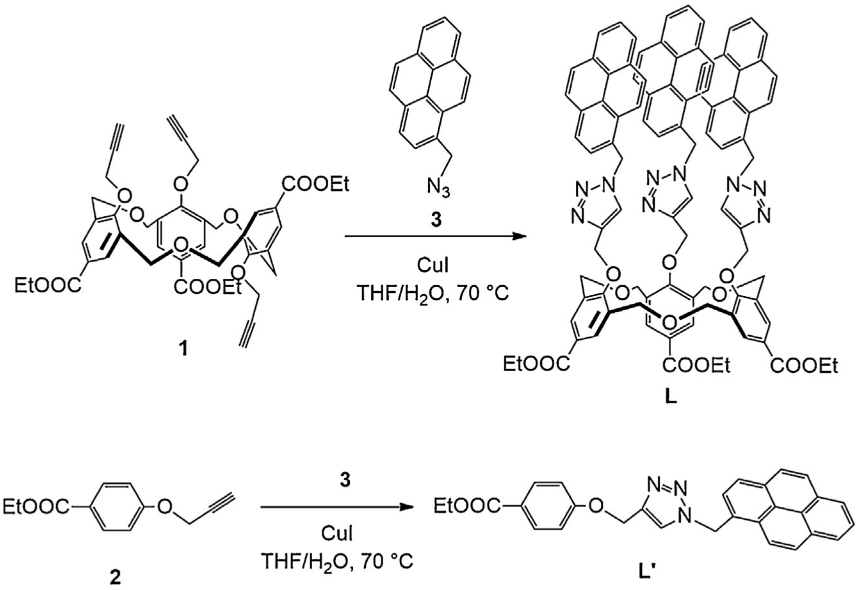
2.2.2. General procedure for synthesis of compound **L′**

Copper iodide (10 mg) was added to compound **2** (200 mg, 0.98 mmol) and 1-azidomethylpyrene (252 mg, 0.98 mmol) in a 30 mL mixture of THF/H_2O (5:1, v/v) and the mixture was heated at 70 °C for 24 h. The resulting solution was cooled and extracted twice with chloroform. The chloroform layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue obtained was purified using a silica gel column eluting with 1:1 hexane/chloroform to give the desired material **L′** (340 mg, 75%) as a white solid. m.p. 153–154 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.34–1.37 (t, 3H, $COOCH_2CH_3$, *J* = 6.8 Hz), 4.29–4.34 (q, 2H, $COOCH_2CH_3$, *J* = 6.8 Hz), 5.13 (s, 2H, ArO—CH_2–triazole), 6.27 (s, 2H, triazole–CH_2–pyrene), 6.89–6.91 (d, 2H, Ar*H*, *J* = 8.4 Hz), 7.37 (s, 1H, triazole–*H*), 7.91–7.93 (d, 2H, Ar*H*, *J* = 8.4 Hz), 7.97–7.99 (d, 1H, pyrene–*H*, *J* = 8.0 Hz), 8.04–8.15 (m, 4H, pyrene–*H*), 8.20–8.26 (m, 4H, pyrene–*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.32, 52.53, 60.62, 61.98, 114.23, 121.78, 122.68, 123.39, 124.41, 124.91, 125.06, 125.85, 125.98, 126.40, 127.15, 127.70, 128.36, 129.13, 129.30, 130.50, 131.12, 131.44, 132.19, 143.76, 161.68, 166.19. FABMS: *m*/*z* 461.17 (M^+). Anal. calcd for $C_{93}H_{75}N_9O_{12}$ (461.51): C 75.47, H 5.02, N 9.10. found: C 75.42, H 5.04, N 9.14.

3. Results and discussion

3.1. Synthesis

The synthetic route for chemosensor **L** is described in Scheme 1. The Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction of com-



Scheme 1. The synthetic route of **L** and **L′**.