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Synthesis and chromic luminescent properties of terbium(III) complexes with novel octopus carboxylates

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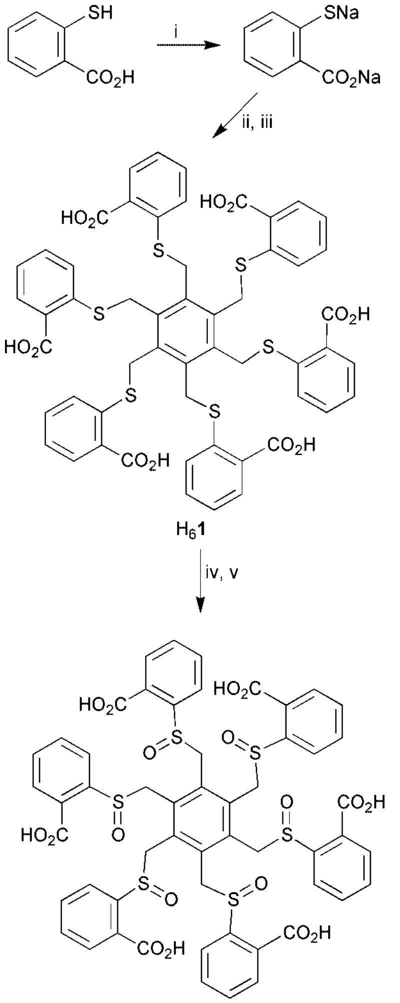
New octopus polythioether 1 and polysulfoxide 2 incorporating rigid Ph–COOH groups, prepared in high yields by a direct and selective procedure, encapsulate terbium(III) ions affording polymeric complexes with interesting vapor-chromic luminescent properties.

Octopus molecules, in particular benzene rings hexasubstituted by flexible side arms with rigid polar groups, show an unusual encapsulating tendency towards metal cations and small guest molecules owing to their conformational mobility which is impeded by spatial crowding.[1,2] Hence, interest has been increasingly attracted to the study of the synthesis and promising application of their metal complexes in the design of supramolecular photonic or electronic devices, catalysts or biomaterials in recent years.[3] Since Vögtle's report of the first octopus ligands and their metal-encapsulating properties,[4] a number of metal complexes with simple octopus ligands, such as hexakis(imidazol-1-ylmethyl)benzene,[5] hexakis(pyrazol-1-ylmethyl)benzene,[6] and hexakis(2-amino-1,3,4-thiadiazol-5-thiomethyl)benzene,[7] have been reported to possess interesting properties. As part of our research for novel lanthanide luminescent materials and our interest in host–guest chemistry we have explored the possibility of incorporating polar groups with large local dipoles serving as hydrogen bond acceptor or redox donors, such as carboxylate and sulfoxide groups, into octopus structures. We present here the synthesis and vapor-chromic luminescent properties of terbium(III) complexes with new octopus polythioether **1** and polysulfoxide **2** containing carboxylate terminal groups. The rigid benzene plane with polar carboxylate or sulfoxide groups, which are capable of hydrogen bond formation in **1** and **2**, assist the capture and stabilization of guest species.

Synthesis of octopuses **1** and **2** is straightforward and high yielding.† Six-fold reaction of hexakis(bromomethyl)benzene[8] with the thiolate anion of 2-mercaptobenzoic acid, which was generated *in situ* using sodium ethoxide in ethanol, proceeds remarkably cleanly to afford the hexamer **1** in >92% yield (Scheme 1). Mild and selective oxidation of **1** in the presence of $KHCO_3$ proceeds to a new octopus polysulfoxide **2** (Scheme 1). The oxidation reaction is carried out by drop-wise addition of bromine in dichloromethane to an aqueous solution of **1** containing 10% of $KHCO_3$ at ~15 °C for 0.5 h.[9] IR ($\nu_{S=O} = 1018\ cm^{-1}$) and ^1H NMR, FAB mass spectroscopy (*m/z* 1171) confirm the formation of analytically pure octopus polysulfoxide **2**.[10]

Terbium(III) complexes with the octopus ligands **1** and **2** were obtained by reaction of the terbium(III) salt of **1** in pyridine or with the sodium salt of **2** in aqueous solution, respectively. Addition of terbium(III) nitrate in methanol to the solution of **1** in pyridine under reflux gives $(Tb_2\mathbf{1})_2Py\cdot 9H_2O$ (**3**) as a white crystalline powder. Reaction of the sodium salt of **2** with $Tb(NO_3)_3\cdot 6H_2O$ in water at room temperature affords $Tb_3\mathbf{2}(OH)_3(H_2O)$ (**4**) as a white solid. Thermal analysis shows total weight losses of 76.0% and 66.5% for **3** and **4** respectively, which correlates well with the expected losses of 75.3% and 67.2%. The IR stretching band of COOH groups appearing at 1686 cm^{-1} in $H_6\mathbf{1}\cdot 6H_2O$ disappears in **3**, while the intense COOH stretching band at 1706 cm^{-1} in $H_6\mathbf{2}\cdot 6H_2O$ shifts to



Scheme 1 Preparation of octopuses **1** and **2**. Reagents and conditions: i. CH_3CH_2ONa/N_2; ii. Hexakis(bromomethyl)benzene/Δ; iii. HCl–H_2O; iv. $Br_2/KHCO_3/CH_2Cl_2$–H_2O; v. HCl–H_2O.

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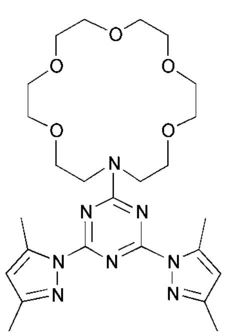

Chart 1

~1659 cm^{-1} as a weak band in **4**. The results indicate that COO groups in **3** are coordinated to Tb^{III} with no hydrogen bonding; while in **4**, some of the coordinated COO groups form H-bonds (probably *via* the non-coordinated O-atom with the H-atom of the ligated OH groups).[11] The strong characteristic S=O stretching band at 1018 cm^{-1} (s) in H_6**2**·$6H_2O$ shifts to 997 cm^{-1} ($\Delta\nu = -21$ cm^{-1}) in **4**. Such a shift reveals that S=O is coordinated to Tb^{III} through O-donor atoms.[12]

In order to investigate the energy transfer effect of the octopus polysulfoxide on lanthanide luminescence, a number of ternary complexes of terbium(III) with the octopus polysulfoxide **2** and dipyrazoltriazine chromophore[13] as co-ligand were prepared and their luminescent properties investigated. Of these, the terbium complex with octopus **2** and adpt, a terpyridine-like ligand incorporating a monoazacrown ether moiety (Chart 1),‡ is demonstrated here. Complex Tb_2(**2**)$(adpt)_2$·$2H_2O$ (**5**) is prepared by reaction of $Tb(NO_3)_3$·$6H_2O$ with **2** and adpt in hot pyridine with high yields. In contrast to complex **4**, the IR spectrum of **5** reveals that the sulfoxide group is not coordinated to Tb ions in **5**, as indicated by a moderate stretching band located at 1019 cm^{-1} corresponding to the free sulfoxide groups. This observation is interesting, because changes of sulfoxide coordination mode should induce local dipole changes, thus affecting the hydrogen-bonding properties of sulfoxide.

Terbium compounds as sensor materials are of special interest for their hypersensitive luminescence properties, since the $^5D_4 \rightarrow {}^7F_J$ transitions of Tb^{III}, which can be sensitized by energy-transfer following excitation of a fully-allowed ligand-based $\pi \rightarrow \pi^*$ transition or a charge transfer band, are sensitive to the micro-environment around Tb.[14] The luminescence spectrum of polycrystalline **3** at 294 K is shown in Fig. 1. The ligand excitation band at 267 nm shifts to a longer wavelength at 362 nm in **3**. The large shift of excitation maximum ($\Delta\lambda_{ex} = \sim 100$ nm) suggests that the aromatic planar arms are assembled around Tb^{III}, resulting in a stacked polymeric structure. Excitation *via* the band at 362 nm gives an emission spectrum displaying the characteristic $^5D_4 \rightarrow {}^7F_J$ transitions of Tb^{III} ions ($\tau(^5D_4) = 1.72$ ms), in which the ligand fluorescence band vanishes completely. This fact implies an efficient conversion of the UV light absorbed by **1** into visible luminescence of Tb^{III} ions, and confirms that all the arms of **1** coordinate to Tb^{III} ions.[15]

Vapor sensitive luminescent probes are of special interest based on their potential applications in environment science and in biotechnology. A number of examples have been reported, such as $[CuI(3\text{-pic})]_x$,[16] $[Au(S_2CN(C_5H_{11})_2)]_2$[17] and $Au_3(CH_3N{=}COCH_3)_3$,[18] showing chromic luminescence sensitive to the volatile organic compounds (VOC). Only very slightly soluble as the polymeric solid **3** is, we found that exposing it to DMF (far less than that needed for substantial dissolution) leads to disappearance of the characteristic luminescence of $^5D_4 \rightarrow {}^7F_J$ and appearance of a broad emission band centered at 419 nm corresponding to ligand luminescence of **1** (Fig. 1). The green luminescence of $^5D_4 \rightarrow {}^7F_J$ can be reversed when adding a small amount of pyridine to the resulting solid. These surprising observations, which are similar to the reported chromic luminescence of $[CuI(3\text{-pic})]_x$,[16] $[Au(S_2CN(C_5H_{11})_2)]_2$[17] and $Au_3(CH_3N{=}COCH_3)_3$,[18] reveal that the solid state coordination environment around Tb^{III} undergoes changes induced by exposure to the two VOCs.

However, the characteristic f→f transitions of Tb^{III} ion is completely vanished in **4**: excitation *via* the ligand band at 266 nm gives emission spectra displaying a characteristic broad band centered at 421 nm which are assigned to the ligand luminescence of **2**. This quenching of the Tb^{III} luminescence suggests the *flexible* coordination environment of Tb ion in **4**, in which coordinated O–H oscillators (COO···H–O, SO···H–O) result in an efficient non-radiative decay of the luminescent ^5D_J level of Tb^{III} ions. Since the weak ligand luminescence was observed, the energy transfer from the organic chromophore to the Tb(III) is partly suppressed in complex **4**. We expect that the terpyridine-like co-ligand containing three nitrogen donors which act as binding sites for the metal cation can efficiently protect the metal from the metal-bound OH oscillators. The ternary complex **5** was thus prepared for comparison. In contrast to compound **4**, ternary complex **5** is brightly green luminescent under UV light (Fig. 2, $\lambda_{ex} = 263$ nm). An interesting chromic luminescence is also observed for **5**: the vapor of acetic acid can quench efficiently the $^5D_4 \rightarrow {}^7F_J$ emission of Tb ion ($\tau(^5D_4) = 2.32$ ms) and lead to a chromic emission band centered at 394 nm corresponding to the ligand emission of adpt (Fig. 2). The hydrogen-bond formation between the uncoordinated SO groups and CH_3COOH molecules may play a role in this chromic luminescence. The green luminescence of **5** was reversed after acetic acid adsorbed in **5** was

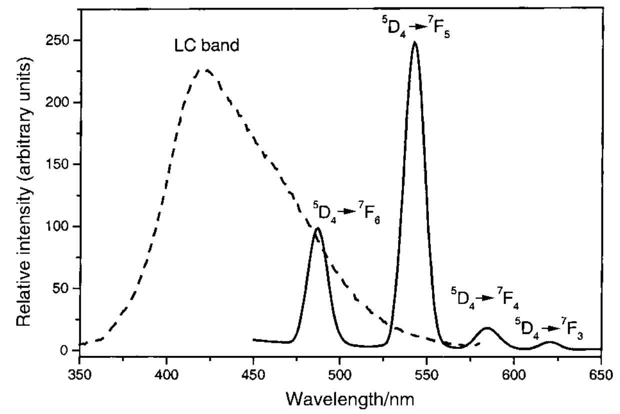

Fig. 1 Luminescence spectrum of microcrystalline **3** at room temperature before (solid line) and after exposure to DMF for 3 minutes (dashed line).

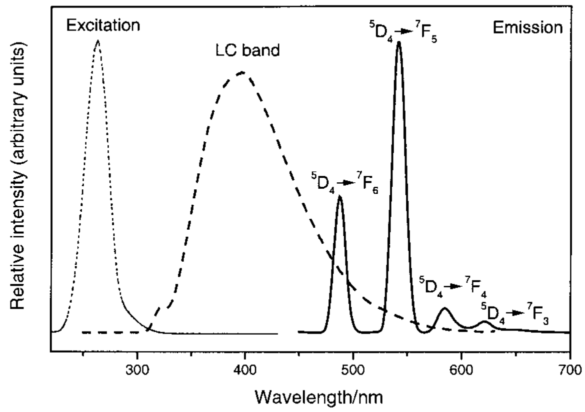

Fig. 2 Luminescence spectrum of film **5** at room temperature before (solid line) and after exposure to CH_3CH_2OH vapor for 5 minutes (LC). The excitation band is shown by the dotted line (left).

evaporated in air for several minutes. Based on the monoazacrown ether moieties incorporated in ligand adpt, compound **5** also displays strong "off–on" switching of the $^5D_4 \rightarrow {}^7F_J$ luminescence with alkali earth cations, and these will be reported later.

In conclusion, novel terbium complexes with octopus carboxylates have been synthesized and their interesting vapor chromic luminescent properties demonstrated. The cavities in the framework of octopus terbium carboxylates and the hydrogen-bonding interactions between sulfoxide groups or COO groups and the guest molecules may be responsible for the observed chromic luminescence.

Acknowledgements

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Notes and references

†Compounds **1–5** gave spectroscopic and analytical data consistent with their structures. *Selected data* for $H_6\mathbf{1}\cdot 6Me_2SO$: colorless prisms, 92% yield, mp 309 °C (decomp.); FAB MS: $m/z = 1075$; δ_H ($(CD_3)_2SO$): 4.31 (s, 2H, SCH_2), 7.20 (t, $J = 7.2$ Hz, 1H, Ph-H^6), 7.34 (q, $J = 7.6$, 2H, Ph-H^4, H^5), 7.86 (d, $J = 7.6$, 1H, Ph-H^3), 13.18 (s, br, 1H, COOH); δ_C ($(CD_3)_2SO$): 124.06, 124.66, 126.52, 128.44, 130.67, 132.56, 135.65, 139.56, 167.53; IR (KBr): 1679, 1586,1564, 1465, 1247, 1148, 1028, 954, 799, 740, 699, 644 cm^{-1}; Anal. Calc. for $C_{66}H_{78}O_{18}S_{12}$: C 51.34, H 5.09, S 24.92; found C 51.39, H 5.10, S 25.08%. For $H_6\mathbf{2}\cdot 6H_2O$: colorless plates, 94% yield, mp 210 °C (decomp.); FAB MS (nba): m/z 1171; IR (KBr): 1706, 1314, 1145, 1060, 1018, 800, 758 and 547 cm^{-1}; δ_H (CD_3OD): 7.67 (m, 24H, Ph), 4.93 (br, 12H, CH_2); Anal. Calc. for $C_{54}H_{54}O_{24}S_6$: C 50.70, H 4.25, S 15.04; found C 50.61, H 4.23, S 14.87%. For **3**: white crystalline powder; IR (KBr): 1589, 1572, 1537, 1463, 1436, 1404, 1060, 1043, 860, 745, 651, 489 cm^{-1}; Anal. Calc. for $Tb_4C_{113}H_{95}NO_{33}S_{12}$: C 45.01, H 3.18, N 0.46, S 12.76; found C 45.05, H 3.21, N 0.50, S 12.63%. For **4**: white solid, 96% yield; IR (KBr): 1588, 1553, 1478, 1412, 1384, 1307, 1050, 997, 806 and 758 cm^{-1}; Anal. Calc. for $Tb_3C_{54}H_{41}O_{22}S_6$: C 37.90, H 2.42, S 11.22; found C 37.86, H 2.42, S 11.27%. For **5**: white powder, 97% yield; IR (KBr): 3388, 2890, 1588, 1553, 1475, 1405, 1307, 1145, 1110, 1089, 1018, 758, and 632 cm^{-1}; Anal. Calc. for $C_{104}H_{114}N_{16}O_{29}S_6Tb_2$: C 48.37, H 4.50, N 8.68, S 7.44; found C 48.48, H 4.49, N 8.71, S 7.39%.

‡Ligand adpt was prepared from starting materials of 2,4,6-trichloro-1,3,5-triazine, 1-aza-18-crown-6 and 3,5-dimethylpyrazole in two steps with 86% general yield. Mp 92–93 °C. δ_H ($CDCl_3$): 2.28 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 3.63 (s, 4H, CH_2), 3.67 (s, 4H, CH_2), 3.76 (t, $J = 5.7$ Hz, 2H, CH_2), 3.99 (t, $J = 5.7$ Hz, 2H, CH_2), 6.03 (s, 1H, Pz-ring H); δ_C($CDCl_3$): 13.69, 15.90, 48.81, 68.90, 70.55, 70.79, 111.16, 124.61, 143.42, 152.02, 163.58; IR (KBr): 3441, 2914, 1607, 1573, 1520, 1400, 1343, 1106, 974, 805, 753 cm^{-1}; Anal. Calc. for $C_{25}H_{38}N_8O_5$: C 56.60, H 7.17, N 21.13; found C 56.51, H 7.19, N 21.25%. FAB MS: $m/z = 531$ [M^+].

1 *Inclusion Compounds*, Eds. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Oxford University Press, Oxford, 1994, vol. 4; G. R. Newkome, C. N. Moorefield and F. Vögtle, *Dendritic Molecules: Concepts, Syntheses and Perspectives*, VCH, New York, 1996.

2 A. D. U. Hardy, D. D. MacNicol and D. R. Wilson, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1011; S. A. Bourne, K. L. G. Nash and F. Toda, *J. Chem. Soc., Perkin Trans. 2*, 1996, 2145.

3 D. D. MacNicol and G. A. Downing, in *Comprehensive Supramolecular Chemistry*, vol. 6, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle and J.-M. Lehn, Pergamon, Oxford, 1996, p. 421; F. Vögtle and E. Weber, *J. Inclus. Phenom. Molec. Recognit. Chem.*, 1992, **12**, 75.

4 F. Vögtle and E. Weber, *Angew. Chem.*, 1974, **86**, 896; *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 814.

5 B. F. Hoskins, R. Robson and D. A. Slizys, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2752.

6 C. M. Hartshorn and P. J. Steel, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2655; C. Foces-Foces, A. L. Llamas-Saiz, R. M. Claramunt, N. Jagerovic, M. L. Jimeno and J. Elguero, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1395.

7 C. Yang, X.-M. Chen, X.-Q. Lu, Q.-H. Zhou and Y.-S. Yang, *Chem. Commun.*, 1997, 2041.

8 J. Zavada, M. Pankova, P. Holy and M. Tichy, *Synthesis*, 1994, 1132.

9 N. Furukawa and H. Fujihara, in *The Chemistry of Sulfones and sulfoxides*, ed. S. Patai, Z. Rappoport and C. J. M. Stirling, John Wiley & Sons Ltd., New York, 1988, p. 541.

10 As the preferred conformation of octopus **1** is "1,3,5-up/2,4,6-down", the major stereoisomers of **2** should be diastereomers. Efforts to isolate the optically pure stereoisomers using TLC and HPLC have been unsuccessful.

11 D. Lin-Vien, N. B. Colthup, W. G. Fateley and J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, NY, 1991.

12 M. Calligaris and O. Carugo, *Coord. Chem. Rev.*, 1996, **153**, 83; J. A. Padies, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 16.

13 C. Yang, X.-M. Chen, W. H. Zhang, J. Chen and Y.-S. Yang, *J. Chem. Soc., Dalton Trans.*, 1996, 1767; C. Yang, X.-M. Chen, Y.-D. Cui and Y.-S. Yang, *Chin. J. Chem.*, 1999, **17**, 411; C. Yang, W.-T. Wong and Y.-S. Yang, *Sci. China (B)*, 2001, **44**, 80.

14 D. Parker, P. K. Senanayake and J. A. G. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2129; V. Balzani, A. Credi and M. Venturi, *Coord. Chem. Rev.*, 1998, **171**, 3; E. B. Van der Tol, H. J. Van Ramesdonk, J. W. Verhoeven, F. J. Steemers, E. G. Kerver, W. Verboom and D. N. Reinhoudt, *Chem. Eur. J.*, 1998, **4**, 2315; N. Fatin-Rouge, E. Toth, D. Perret, R. H. Backer, A. E. Merbach and J.-C. G. Bunzli, *J. Am. Chem. Soc.*, 2000, **122**, 10810.

15 C. Piguet and J.-C. G. Bunzli, *Chem. Soc. Rev.*, 1999, **28**, 347; N. Sabbatini, M. Guardigli and J.-M. Lehn, *Coord. Chem. Rev.*, 1993, **123**, 201; G. Ulrich, R. Ziessel, I. Manet, M. Guardigli, N. Sabbatini, F. Fraternali and G. Wipff, *Chem. Eur. J.*, 1997, **3**, 1815.

16 E. Cariati, J. Bourassa and P. C. Ford, *Chem. Commun.*, 1998, 1623.

17 M. A. Mansour, W. B. Connick, R. J. Lachicotte, H. J. Gysling and R. Eisenberg, *J. Am. Chem. Soc.*, 1998, **120**, 1329.

18 J. C. Vickery, M. M. Olmstead, E. Y. Fung and A. L. Balch, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1179.