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Sulfate Binding with a Tripodal Tris(4-pyridylurea) Receptor

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The tris(2-aminoethyl)amine (tren)-based tris(4-pyridylurea) receptor **L** has been synthesized and its anion binding properties were studied. The ligand forms a 2∶1 (host/guest) complex with $MgSO_4$, $[SO_4^{2-}\subset\mathbf{L}_2]$, in which a sulfate ion is encapsulated by six urea groups from the two ligands through multiple hydrogen bonds. The metal ions do not coordinate to the pyridyl groups but exist as the hydrate $[Mg(H_2O)_6]^{2+}$ and interact with the $[SO_4\subset\mathbf{L}_2]$ capsules in the outer coordination sphere to form a three dimensional extended structure. The anion binding behavior of ligand **L** in solution was studied.

Keywords anion binding, tripodal tris(4-pyridylurea), sulfate, capsule

Introduction

Anion coordination chemistry has been an important research topic due to the relevance of anions in many fields such as life science, medicine, catalysis, and environmental chemistry.[1] A wide variety of hydrogen donor groups, such as ammonium, guanidine, pyrrole, indole, amide, and urea/thiourea units have been incorporated into different backbones for the binding and recognition of anions.[2-4] In particular, urea-based ligands have attracted much interest because of their ability to bind anions, from the spherical halides to the tetrahedral oxoanions, with double H-bond motifs.[5]

The tripodal, tren-based tris(urea) receptors display an excellent shape complementarity to tetrahedral anions and are therefore very promising for the binding and extraction of sulfate anion, which is of importance in environmental remediation and nuclear waste cleanup.[6] A number of such ligands have been synthesized with different functional substituents, and their binding properties toward inorganic anions like Cl^-, PO_4^{3-} and SO_4^{2-} have been thoroughly investigated.[7-17] For example, the *meta*-cyanophenyl-appended tripodal tris (urea) ligand forms a silver-based MOF that encapsulates the SO_4^{2-} ion by twelve hydrogen bonds from two ligands.[8b] The 4-nitrophenyl and pentafluorophenyl-functionalized ligands show selectivity toward halides and oxyanions.[9,10] Recently, Wang *et al*.[12] reported the squaramide-based tripodal anion receptors which can selectively encapsulate SO_4^{2-} ion, and Frontera *et al*.[13] reported the squaramide-ammonium-based tripodal receptors for carboxylate anion binding.

We have reported a tris(3-pyridylurea) ligand ($\mathbf{L}^{3\text{-py}}$) that can selectively encapsulate a sulfate ion with one or two ligands in different second-sphere, hydrogen-bonded networks.[14] Moreover, the tripodal tris(urea) ligand has been modified with ferrocenyl groups ($\mathbf{L}^{Fc}$)[15] and quinolinyl ($\mathbf{L}^{Qn}$)[16] or $Ru(bipy)_3$[17] moieties for the electrochemical or fluorescent signaling purposes. The results further demonstrate the excellent affinity and selectivity of tripodal tris(urea) ligands for sulfate and phosphate ions. It is noticeable that the 3-pyridyl substituents do not coordinate to the metal ions in the sulfate complexes; instead, the metal ions exist as $[M(H_2O)_6]^{2+}$.[11,14a] In order to further study the anion coordination properties of tripodal tris(urea) ligands and to explore the effects of the potentially metal-coordinating pyridyl substituents on the structure of the anion complexes, we synthesized an analogous ligand, the tripodal tris(4-pyridylurea) (**L**), and now report the sulfate ion encapsulation by ligand **L** in the complex $[Mg(H_2O)_6][SO_4\subset\mathbf{L}_2]$ (**1**) (Scheme 1).

Experimental

General

^1H and ^{13}C NMR spectra were measured with a Varian unity INOVA-400 spectrometer with calibration against the solvent signal (DMSO-d_6: δ 2.50 for ^1H NMR) or tetramethylsilane (TMS). Elemental analyses were done on a VarioEL III Elemental Analyzer.

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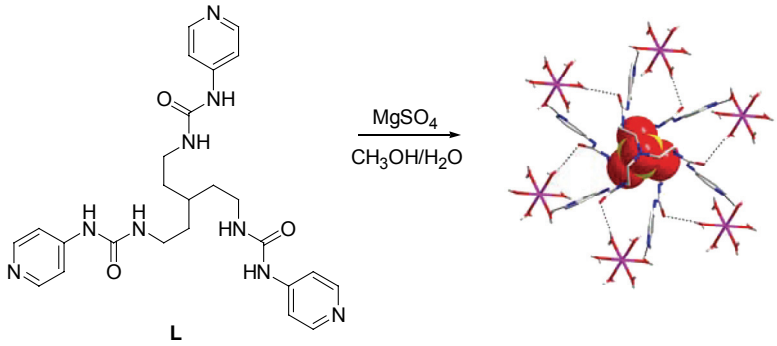
Scheme 1 Self-assembly of ligand **L** with $MgSO_4$



Melting points were detected on an X-4 Digital Vision MP Instrument. ESI-MS measurements were performed on a MALDI-TOF Mass Spectrometer. IR spectra were obtained on a Bruker EQUINOX-55 FTIR spectrometer as KBr pallets.

Synthesis of ligand L and the sulfate complex 1

A solution of isonicotinic acid acyl azide (1.23 g, 8.0 mmol; see Supporting Information for the synthesis) in toluene (80 mL) was refluxed under nitrogen for 1 h, and tris(2-aminoethyl)-amine (tren) (0.33 g, 2.0 mmol) in toluene (25 mL) was added dropwise. The mixture was stirred for another 1 h and cooled to room temperature. The crude product was purified by recrystallization from CH_3OH/H_2O (V : V=1 : 4) to give **L** as a white solid. Yield 0.47 g, 46%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 2.60 (t, J=6.4 Hz, 6H, NCH_2), 3.18−3.21 (m, 6H, CH_2), 6.36 (t, J=4.8 Hz, 3H, NH), 7.34 (d, J=5.2 Hz, 3H, H1), 8.26 (d, J=5.2 Hz, 3H, H2), 9.01 (s, 3H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 37.6, 53.6, 147.2, 111.9, 150.0, 154.8; FT-IR (KBr) ν: 3328, 3266, 2837, 1691, 1589, 1527, 1416, 1200, 822 cm^{-1}; Anal. calcd for $C_{24}H_{30}N_{10}O_3$ (506.56): C 56.90, H 5.97, N 27.65; found C 57.10, H 5.92, N 27.56; ESI-MS m/z: 505.5 ([**L**+H]$^+$).

A methanol solution (2 mL) of **L** (25 mg, 0.05 mmol) and an aqueous solution (0.5 mL) of $MgSO_4$ (3 mg, 0.025 mmol) were mixed and the trace precipitate was removed by filtration. Slow diffusion of diethyl ether into the filtrate for several days gave colorless crystals of complex $[Mg(H_2O)_6][SO_4\mathbf{L}_2]$ (**1**). Yield 28 mg, 90%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 2.42 (t, J=6.0 Hz, 6H, NCH_2), 3.08−3.10 (m, 6H, CH_2), 7.65 (t, J=4.8 Hz, 3H, NH), 7.46 (d, J=5.6 Hz, 3H, H1), 8.11 (d, J=5.6 Hz, 3H, H2), 9.90 (s, 3H, NH); FT-IR (KBr) ν: 3299, 2810, 1689, 1540, 1250, 1208, 1101 (SO_4^{2-}), 992, 810 cm^{-1}; Anal. calcd for $[Mg(H_2O)_6][SO_4\mathbf{L}_2]$: C 44.16, H 5.56, N 21.46; found C 44.21, H 5.51, N 21.43; ESI-MS m/z: 505.2 ([**L**–H]$^-$), 554.6 ([2**L**+SO_4]$^{2-}$), 603.2 ([**L**+HSO_4]$^-$).

X-ray crystallography

Diffraction data for receptor **L** and complex **1** were collected on a Bruker SMART APEX II diffractometer at room temperature (292 K) with graphite-monochromated Mo Kα radiation (λ=0.71073 Å). Empirical absorption correction by using SADABS was applied for all data. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2. Hydrogen atoms bonded to carbon and nitrogen atoms were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. CCDC-935225 (**L**) and 935226 (**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **L**: $C_{24}H_{31}N_{10}O_{3.50}$ (515.59), colorless, block, monoclinic, space group $C2/c$, a=25.391(4) Å, b=9.8909(17) Å, c=20.453(4) Å, β=94.59(3)°, V=5120.0(15) Å^3, T=296(2) K, Z=8, D_{calcd}=1.338 g•cm^{-3}, F_{000}=2184, μ=0.09 mm^{-1}, 15188 reflections collected, 6187 unique (R_{int}=0.0248), no. of observed reflections 4461 ($I>2\sigma(I)$), R_1=0.0719, wR_2=0.2207.

Crystal data for **1**: $C_{48}H_{72}MgN_{20}O_{20}S$ (1305.63), colorless block, rhombohedral, space group R-3, $a=b$=13.7339(17) Å, c=28.756(3) Å, V=4697.3(9) Å^3, T=293(2) K, Z=3, D_{calcd}=1.385 g•cm^{-3}, F_{000}=2064, μ=0.15 mm^{-1}, 7783 reflections collected, 1837 unique (R_{int}=0.0599), no. of observed reflections 1468 ($I>2\sigma(I)$), R_1=0.0845, wR_2=0.2594.

Results and Discussion

Syntheses and crystal structures

The receptor **L** was synthesized in moderate yield by a three step process (Scheme S1). The free ligand crystallizes in the space group $C2/c$. In the structure, two urea arms form the typical intramolecular N−H···O hydrogen bonds between the NH groups and carbonyl (Figure S7 and Table S1). Moreover, intermolecular urea···urea hydrogen bonds lead to an infinite 1D chain (Figure S8) which is similar to the analogous tris(3-pyridylurea)[14a] and other known tripodal tris(urea) ligands.[15,16]

The binding of **L** with sulfate anion was tested by using various sulfate salts. The complex $[Mg(H_2O)_6]$•

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$[SO_4\subset\mathbf{L}_2]$ (**1**) was obtained by slow diffusion of diethyl ether to a CH_3OH/H_2O solution of the ligand and $MgSO_4$. Under similar conditions, crystals were also isolated from **L** and the zinc(II) and manganese(II) sulfate, and preliminary structures display a similar sulfate capsule as in complex **1**. Unfortunately, the crystal data are too poor to allow for a satisfactory refinement of the structures.

Complex **1** crystallizes in the rhombohedral *R*-3 space group, which is different from the analogous sulfate complexes of the 3-pyridyl-substituted tris(urea) ligand, $[M(H_2O)_6][SO_4\subset(\mathbf{L}^{3\text{-py}})_2]$ (M=Mg, Zn, Mn, Cd, Co) (monoclinic space group $P2_1/n$).[11,14a] In the structure of complex **1**, the ligand molecule displays the C_3 symmetry, which also differs from the complexes of $\mathbf{L}^{3\text{-py}}$. Nevertheless, the main structure of **1** is similar to the latter complexes, with a sulfate ion being encapsulated in a cavity formed by two inversion-symmetric molecules of ligand **L** through multiple hydrogen bonds (Figure 1). The separation between the two bridgehead N atoms in **1** (9.990 Å) is slightly longer than that of the complex of $\mathbf{L}^{3\text{-py}}$ (9.667 Å). As in the case of the $\mathbf{L}^{3\text{-py}}$ complexes, due to the inversion symmetry, each oxygen atom of the sulfate ion is distributed to two positions (Figure 1d) to form a cube.

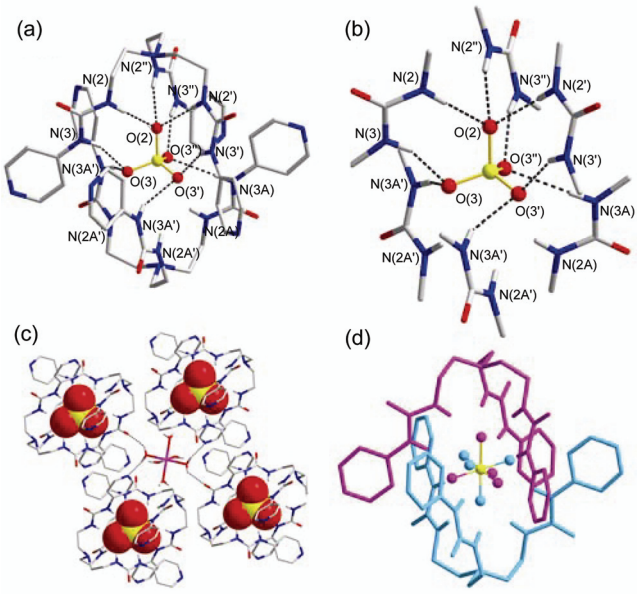

Figure 1 Crystal structure of complex **1**. (a) The sulfate capsule $[SO_4^{2-}\subset\mathbf{L}_2]$; (b) Coordination of SO_4^{2-} ion by six urea groups; (c) Extended structure showing the $[Mg(H_2O)_6]^{2+}$ unit surrounded by $[SO_4^{2-}\subset\mathbf{L}_2]$ capsules; (d) Two inversion-related **L** molecules and the disordered sulfate ion.

The most important structural feature of **1**, however, is the sulfate coordination by the ligands. Previous theoretical calculations and experiments proved that the tetrahedral sulfate ion can reach a saturated coordination of twelve hydrogen bonds, which can be provided by six urea groups.[8b,18] In our recently reported analogous complex of $\mathbf{L}^{3\text{-py}}$, although the sulfate ion is surrounded by six urea groups, there are eleven stronger N—H···O hydrogen bonds (N···O distance <3.2 Å) plus five weaker ones (N···O distance <3.5 Å) for the sulfate ion. In the present complex **1** (with the 4-pyridyl substituted ligand **L**), the situation is again different: the sulfate ion is coordinated by a total of eighteen hydrogen bonds, nine with N···O distance <3.2 Å and nine in the range 3.2—3.5 Å (Table 1, Figure 1a). This deviation from the twelve hydrogen-bond coordination and formation of relatively weaker hydrogen bonds may be attributed to the fact that one of the ligand molecules is less complementary for the optimal binding, *i.e.* chelating the edges of the tetrahedral anion.

Table 1 Hydrogen bonds (Å) and angles (°) around the SO_4^{2-} ion in **1**

D—H···A	*d*(N—H)	*d*(H···O)	*d*(N···O)	∠(NHO)
N(2)—H(2)···O(2)	0.86	2.20	3.041(6)	165
N(3)—H(3)···O(2)	0.86	2.74	3.488(3)	146
N(3)—H(3)···O(3)	0.86	2.01	2.798(6)	155
N(3A')—H(3A')···O(3)	0.86	2.32	3.124(8)	156
N(2A')—H(2A')···O(3)	0.86	2.63	3.370(7)	144
N(3A")—H(3A")···O(3)	0.86	2.55	3.295(8)	145

Symmetry codes: (A) $-x, -y, -z$; (A') $y, -x+y, -z$; (A") $x-y, x, -z$.

As in the analogous complex of $\mathbf{L}^{3\text{-py}}$, the 4-pyridyl groups in ligand **L** do not coordinate to the metal ions either. They are also involved in second-sphere coordination with water molecules of the hydrated cation $[Mg(H_2O)_6]^{2+}$ through O—H···N hydrogen bonding interactions. Each $[SO_4\subset\mathbf{L}_2]$ capsule is located in the center of an octahedron formed by six $[Mg(H_2O)_6]^{2+}$ cations via six Ow—H···N and six Ow—H···O interactions (Figure S9a), while each $[Mg(H_2O)_6]^{2+}$ cation is also surrounded by six $[SO_4\subset\mathbf{L}_2]$ units in an octahedron (Figure S9b), resulting in a NaCl-type structure as in the case of $\mathbf{L}^{3\text{-py}}$.[11,14a]

Complex **1** was further characterized by the IR spectrum, which shows the stretching vibration peak of sulfate at 1100 cm^{-1} (Figure S5). Moreover, the powder XRD spectrum of the bulk sample matches well with the diffraction patterns simulated from the structure of complex **1** (Figure S6).

Solution anion binding studies

^1H NMR spectrum of complex **1** (Figure S4) showed significant downfield shifts ($\Delta\delta$=1.29 and 0.89) of the two urea NH protons relative to the free ligand **L** in DMSO-d_6, indicating strong binding for sulfate ion. The CH protons also display slight changes. ESI-MS spectrum (negative mode) of complex **1** (Figure 2) displays anionic peaks at *m*/*z* 554.6 for the divalent $[2\mathbf{L}+SO_4]^{2-}$ and 603.2 for $[\mathbf{L}+HSO_4]^-$ (calculated 554.2 and 603.4, respectively), suggesting that the $[SO_4\subset\mathbf{L}_2]$ capsule can persist in solution.

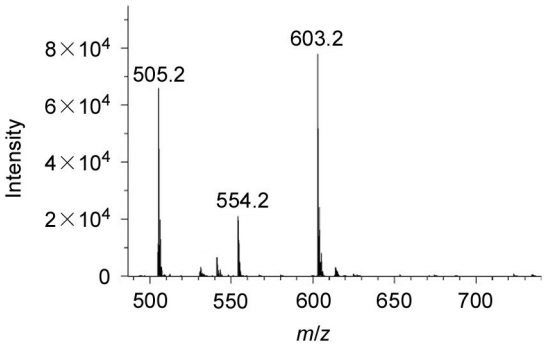

Figure 2 ESI-MS spectrum (negative mode) of complex **1**.

The solution binding behavior of ligand **L** with various anions was studied by ^{1}H NMR spectroscopy in DMSO-d_6/0.5% water (Figure 3). The tetrabutylammonium salts of NO_3^-, ClO_4^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, SO_4^{2-} ions were used in the investigations. Upon addition of 1.0 equiv. of AcO^-, Cl^-, $H_2PO_4^-$, HSO_4^-, and SO_4^{2-} anions, the two NH signals of ligand **L** showed significant downfield shifts. In particular, the SO_4^{2-} anion induced the largest downfield shifts of NH protons ($\Delta\delta$(NHa)=2.16, $\Delta\delta$(NHb)=1.60), indicating strong binding affinity for sulfate. On the other hand, addition of Br^-, I^-, NO_3^-, and ClO_4^- ions resulted in almost no change.

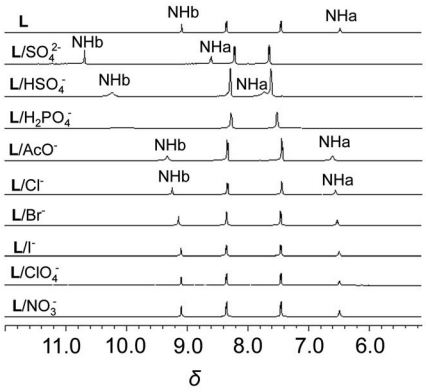

Figure 3 ^{1}H NMR spectra of **L** (5 mmol•L^{-1}) in the presence of 1.0 equiv. of various anions (added as Bu_4N^+ salts, DMSO-d_6, 400 MHz).

^{1}H NMR titration of sulfate ions to ligand **L** was carried out. With the addition of SO_4^{2-} ions (as Bu_4N^+ salt, 0 to 5 equiv.), the urea NH signals displayed gradual downfield shifts, and the spectrum reached saturation with 1.2 equiv. of SO_4^{2-} ions, indicating a 1∶1 binding mode in solution (Figure 4). The aromatic region (protons H3, H4) showed only very slight changes. The 1∶1 binding stoichiometry in DMSO-d_6 was further verified by the Job's plot analysis (Figure S10). It is noticeable that this binding ratio is different from the 2∶1 complex **1** in the solid state, and such a difference between solid-state and solution binding has also been observed for many receptors.[8a,19] However, the sulfate capsule could also be detected in the ESI-MS spectrum of complex **1** with the $[Mg(H_2O)_6]^{2+}$ countercation. The sulfate ion binding constant (lg K=3.77, Figure S11) was obtained by fitting the ^{1}H NMR titration data with the EQNMR program.[20] This affinity is comparable to the reported phenyl-substituted tripodal urea receptor (lg K=3.48).[7a]

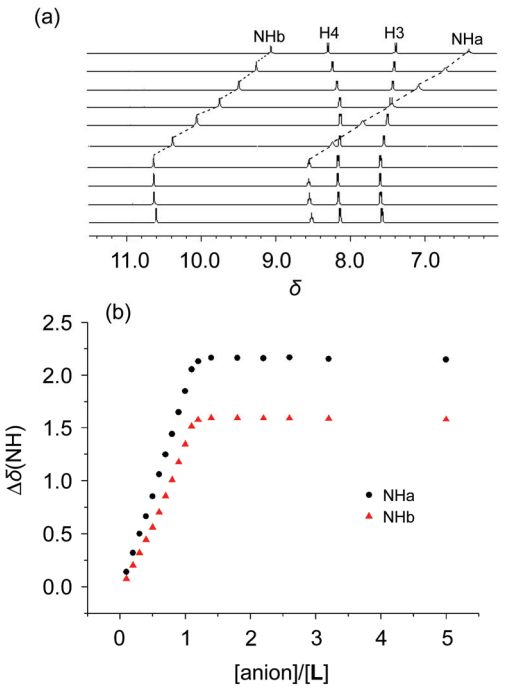

Figure 4 (a) Partial ^{1}H NMR spectra during the titration of **L** (5 mmol•L^{-1}) with [n-$Bu_4N]_2SO_4$ (from up to bottom, the dosage is 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 2.2, 5.0 equiv.) in DMSO-d_6; (b) ^{1}H NMR titration curves of **L** with [n-$Bu_4N]_2SO_4$ in DMSO-d_6 showing the changes in the chemical shifts of NHa and NHb.

Conclusions

In summary, the tren-based tris(4-pyridylurea) receptor (**L**) was synthesized. Assembly of **L** with sulfate salts (*e.g.* $MgSO_4$) led to the anion complex $[Mg(H_2O)_6][SO_4\subset\mathbf{L}_2]$, in which a sulfate ion is encapsulated by two **L** molecules through multiple hydrogen bonds from six urea groups. The pyridyl groups do not coordinate to the metal ions; instead, they contact with the $[Mg(H_2O)_6]^{2+}$ cations through hydrogen bonds in the second coordination sphere, resulting in a three-dimensional structure. ^{1}H NMR and ESI-MS studies confirm the binding affinity and selectivity of sulfate ion.

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References

[1] (a) Sessler, J. L.; Gale, P. A.; Cho, W.-S. *Anion Receptor Chemistry*,

Royal Society of Chemistry, Cambridge, **2006**; (b) Wenzel, M.; Hiscock, J. R.; Gale, P. A. *Chem. Soc. Rev.* **2012**, *41*, 480; (c) Gale, P. A.; Quesada, R. *Coord. Chem. Rev.* **2006**, *250*, 3219; (d) Steed, J. W. *Chem. Soc. Rev.* **2009**, *38*, 506; (e) Amendola, V.; Fabbrizzi, L. *Chem. Commun.* **2009**, 513; (f) Pérez, J.; Riera, L. *Chem. Soc. Rev.* **2008**, *37*, 2658; (g) Blondeau, P.; Segura, M.; Pérez-Fernández, R.; De Mendoza, J. *Chem. Soc. Rev.* **2007**, *36*, 198.

[2] (a) Lakshminarayanan, P. S.; Suresh, E.; Ghosh, P. *Inorg. Chem.* **2006**, *45*, 4372; (b) Berrocal, M. J.; Cruz, A.; Badr, I. H. A.; Bachas, L. G. *Anal. Chem.* **2000**, *72*, 5295; (c) Turner, D. R.; Paterson, M. J.; Steed, J. W. *J. Org. Chem.* **2006**, *71*, 1598; (d) Lakshminarayanan, P. S.; Ravikumar, I.; Suresh, E.; Ghosh, P. *Chem. Commun.* **2007**, 5214; (e) Wang, D. Y.; Wang, J. L.; Zhang, D. W.; Li, Z. T. *Sci China, Chem.* **2012**, *55*, 2018.

[3] (a) Eller, L. R.; Stępień, M.; Fowler, C. J.; Lee, J. T.; Sessler, J. L.; Moyer, B. A. *J. Am. Chem. Soc.* **2007**, *129*, 11020; (b) Borman, C. J.; Custelcean, R.; Hay, B. P.; Bill, N. L.; Sessler, J. L.; Moyer, B. A. *Chem. Commun.* **2011**, *47*, 7611; (c) Gale, P. A.; Hiscock, J. R.; Jie, C. Z.; Hursthouse, M. B.; Light, M. E. *Chem. Sci.* **2010**, *1*, 215; (d) Kim, J.-I.; Juwarker, H.; Liu, X.; Lah, M. S.; Jeong, K.-S. *Chem. Commun.* **2010**, *46*, 764; (e) Kang, S. O.; Begum, R. A.; Bowman-James, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7882.

[4] (a) Custelcean, R.; Bosano, J.; Bonnesen, P. V.; Kertesz, V.; Hay, B. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 4025; (b) Amendola, V.; Fabbrizzi, L.; Mosca, L. *Chem. Soc. Rev.* **2010**, *39*, 3889; (c) Jia, C.; Wu, B.; Li, S.; Huang, X.; Yang, X.-J. *Org. Lett.* **2010**, *12*, 5612; (d) Jia, C.; Wu, B.; Li, S.; Yang, Z.; Zhao, Q.; Liang, J.; Li, Q.-S.; Yang, X.-J. *Chem. Commun.* **2010**, *46*, 5376; (e) Dos Santos, C. M. G.; Boyle, E. M.; De Solis, S.; Kruger, P. E.; Gunnlaugsson, T. *Chem. Commun.* **2011**, *47*, 12176.

[5] (a) Steed, J. W. *Chem. Soc. Rev.* **2010**, *39*, 3686; (b) Li, A.-F.; Wang, J.-H.; Wang, F.; Jiang, Y.-B. *Chem. Soc. Rev.* **2010**, *39*, 3729; (c) Bondy, C. R.; Loeb, S. J. *Coord. Chem. Rev.* **2003**, *240*, 77; (d) Marivel, S.; Arunachalam, M.; Ghosh, P. *Cryst. Growth Des.* **2011**, *11*, 1642; (e) Ravikumar, I.; Ghosh, P. *Chem. Commun.* **2010**, *46*, 1082.

[6] (a) Cameron, B. R.; Loeb, S. J. *J. Chem. Soc., Chem. Commun.* **1997**, 573; (b) Moyer, B. A.; Delmau, L. H.; Fowler, C. J.; Ruas, A.; Bostick, D. A.; Sessler, J. L.; Katayev, E.; Pantos, G. D.; Llinares, J. M.; Hossain, M. A.; Kang, S. O.; Bowman-James, K. In *Advances in Inorganic Chemistry*, Vol. 59, Eds: van Eldik, R.; Bowman-James, K., Elsevier, Oxford, **2006**, pp. 175—204.

[7] (a) Raposo, C.; Almaraz, M.; Martin, M.; Weinrich, V.; Mussons, M. L.; Alcazar, V.; Caballero, M. C.; Moran, J. R. *Chem. Lett.* **1995**, 759; (b) Loos, M. D.; Ligtenbarg, A. G. J.; Esch, J. V.; Kooijman, H.; Spek, A. L.; Hage, R.; Kellogg, R. M.; Feringa, B. L. *Eur. J. Org. Chem.* **2000**, 3675; (c) Han, J.; Deng, C.; Fang, R.; Li, Y. Z.; Wang, L. Y.; Pan, Y. *Sci. China, Chem.* **2010**, *53*, 851.

[8] (a) Pramanik, A.; Thompson, B.; Hayes, T.; Tucker, K.; Powell, D. R.; Bonnesen, P. V.; Ellis, E. D.; Lee, K. S.; Yu, H.; Hossain, M. A. *Org. Biomol. Chem.* **2011**, *9*, 4444; (b) Custelcean, R.; Moyer, B. A.; Hay, B. P. *Chem. Commun.* **2005**, 5971.

[9] Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Inorg. Chem.* **2007**, *46*, 5817.

[10] Ravikumar, I.; Lakshminarayanan, P. S.; Arunachalam, M.; Suresh, E.; Ghosh, P. *Dalton Trans.* **2009**, 4160.

[11] (a) Custelcean, R.; Remy, P.; Bonnesen, P. V.; Jiang, D.-E.; Moyer, B. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 1866; (b) Custelcean, R.; Bock, A.; Moyer, B. A. *J. Am. Chem. Soc.* **2010**, *132*, 7177.

[12] Jin, C.; Zhang, M.; Wu, L.; Guan, Y. F.; Pan, Y.; Jiang, J. L.; Lin, C.; Wang, L. Y. *Chem. Commun.* **2013**, *49*, 2025.

[13] (a) Frontera, A.; Morey, J.; Oliver, A.; Piña, M. N.; Quiñonero, D.; Costa, A.; Ballester, P.; Deyà, P. M.; Anslyn, E. V. *J. Org. Chem.* **2006**, *71*, 7185; (b) Quiñonero, D.; López, K. A.; Deyà, P. M.; Piña, M. N.; Morey, J. *Eur. J. Org. Chem.* **2011**, 6187.

[14] (a) Wu, B.; Liang, J.; Yang, J.; Jia, C.; Yang, X.-J.; Zhang, H.; Tang, N.; Janiak, C. *Chem. Commun.* **2008**, 1762; (b) Zhuge, F.; Wu, B.; Liang, J.; Yang, J.; Liu, Y.; Jia, C.; Janiak, C.; Tang, N.; Yang, X.-J. *Inorg. Chem.* **2009**, *48*, 10249.

[15] Li, M.; Wu, B.; Jia, C.; Huang, X.; Zhao, Q.; Shao, S.; Yang, X.-J. *Chem. Eur. J.* **2011**, *17*, 2272.

[16] Hao, Y.; Jia, C.; Lia, S.; Huang, X.; Yang, X.-J.; Janiak, C.; Wu, B. *Supramol. Chem.* **2012**, *24*, 88.

[17] Hao, Y.; Yang, P.; Li, S.; Huang, X.; Yang, X.-J.; Wu, B. *Dalton Trans.* **2012**, *41*, 7689.

[18] (a) Gao, B.; Liu, Z.-F. *J. Chem. Phys.* **2004**, *121*, 8299; (b) Hay, B. P.; Firman, T. K.; Moyer, B. A. *J. Am. Chem. Soc.* **2005**, *127*, 1810.

[19] (a) Wei, M.; Wu, B.; Zhao, L.; Zhang, H.; Li, S.; Zhao, Y.; Yang, X.-J. *Org. Biomol. Chem.* **2012**, *10*, 8758; (b) Wang, J.; Li, S.; Yang, P.; Huang, X.; Yang, X.-J.; Wu, B. *CrystEngComm* DOI: 10.1039/C3CE26982E.

[20] Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311.

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