ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 8605–8607

www.rsc.org/chemcomm

COMMUNICATION

Highly fluorescent M_2L_4 molecular capsules with anthracene shells†

Zhiou Li,[a] Norifumi Kishi,[a] Kimiko Hasegawa,[b] Munetaka Akita[a] and Michito Yoshizawa*[a]

Received 19th May 2011, Accepted 14th June 2011
DOI: 10.1039/c1cc12946e

M_2L_4 molecular capsules self-assembled from M(II) ions (where M = Zn, Ni, and Pd) and bent bidentate ligands constructed from anthracene fluorophores. The Ni(II) and Zn(II) capsules exhibited weak to strong blue emission unlike traditional Pd(II) cages and capsules.

Fluorescence has widespread applications from fundamental sciences to practical materials and devices. Host–guest interactions within the well-defined cavities of self-assembled, nanometre-sized coordination capsules portend practical applications as chemosensors, biological probes, and light-emitting diodes.[1,2] However, nearly all capsules and cages composed of reversible metal–ligand bonds are non-emissive due to quenching by the heavy transition metal ions.[3] The few coordination capsules assembled using Cd(II), Hg(II), or Zn(II) ions can exhibit weak or moderate emission from the typically small, aromatic ligand frameworks.[4,5] Here we describe highly fluorescent M_2L_4 coordination capsule $\mathbf{1}^{\mathbf{Zn}}$, quantitatively self-assembled from Zn(II) ions and bent bidentate ligand **2** with expanded aromatic surfaces (Fig. 1). The eight anthracene panels define and enclose a large interior cavity, ~1 nm in diameter. In sharp contrast to non-emissive traditional Pd(II) cages and capsules,[3] the Zn(II) capsule shows strong blue emission, λ_{max} = 438 nm and Φ_F = 0.81 and, surprisingly, the Ni(II) capsule was also found to be emissive, Φ_F = 0.20.

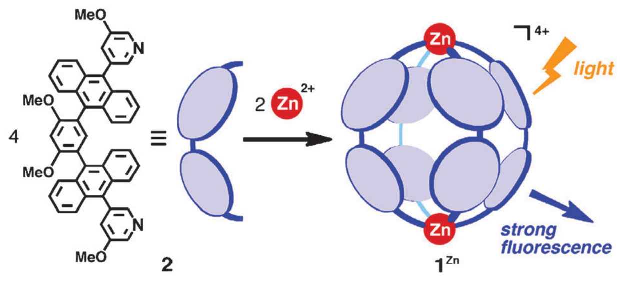

Fig. 1 Design of highly fluorescent Zn(II)-linked molecular capsule $\mathbf{1}^{\mathbf{Zn}}$ assembled from two Zn(II) ions and four bidentate ligands **2** consisting of large anthracene panels.

Anthracenes are a well-known class of highly emissive fluorophores,[6,7] yet the incorporation of anthracenes or other similar, highly emissive large aromatics into the framework of discrete coordination cages to install desirable photophysical properties has yet to be reported.[8] We recently succeeded in the preparation of M_2L_4 molecular capsule $\mathbf{1}^{\mathbf{Pd}}$ by using Pd(II) ions and analogous bidentate ligand **2**.[9] The Pd(II) capsule contains eight anthracene fluorophores but no emission was observed. In a manner similar to other coordination hosts, quenching likely occurs *via* the prerequisite transition metal ions.[3,10] To engender potentially useful emissive properties in M_2L_4 coordination capsules, Zn(II) ions were employed as the metal hinges as their fully occupied d^{10} electronic configuration is generally more tolerant of emission from nearby fluorophores.[4] $Zn(OTf)_2$ proved to be the best source of the Zn(II) hinge and we were delighted to find that simply switching from Pd(II) to Zn(II) provided the highly fluorescent M_2L_4 coordination capsule (Fig. 1).

Zn(II)-linked molecular capsule $\mathbf{1}^{\mathbf{Zn}}$ formed quantitatively upon mixing ligand **2**[11] (17.0 μmol) and $Zn(OTf)_2$ (8.50 μmol) in CD_3CN (0.5 mL) at 80 °C for 1 h (Fig. 2). In the ^1H NMR spectrum (Fig. 2b and c), the two signals of the peripheral pendant methoxy groups H_k and H_j were clearly observed (at 4.22 and 3.91 ppm, respectively) where only H_k displayed a significant downfield shift ($\Delta\delta = +0.34$ ppm) upon the capsule formation.[12] Eleven proton signals were observed for anthracene ($H_{c,c',d,d',e,f}$), pyridine ($H_{g,h,i}$), and *m*-phenylene ($H_{a,b}$) rings in the aromatic region (Fig. 2c). The large upfield shift of H_b on the central *m*-phenylene ring ($\Delta\delta = -1.34$ ppm) is indicative of a capsule structure and increased shielding from the flanking anthryl moieties. Upon heating (~50 °C), Zn(II) capsule $\mathbf{1}^{\mathbf{Zn}}$ remained intact and the broad proton signals became relatively sharp (Fig. S11b, ESI†). At low temperature (0 °C), they resolved into two sharp signals, indicating that the motion of the anthracene panels was suppressed. The diameter of the capsule was calculated to be approximately 1.6 nm on the basis of the single band at $\log D = -9.1$ ($D = 7.5 \times 10^{-10}$ m^2 s^{-1}) in the ^1H DOSY NMR spectrum (Fig. S12, ESI†).[12] The ESI-TOF MS spectrum of a CH_3CN solution of $\mathbf{1}^{\mathbf{Zn}}$ unambiguously confirmed the M_2L_4 composition with prominent signals at *m*/*z* = 737.5 ($[\mathbf{1}^{\mathbf{Zn}} - 4{\cdot}TfO^-]^{4+}$), 747.7 ($[\mathbf{1}^{\mathbf{Zn}} + CH_3CN - 4{\cdot}TfO^-]^{4+}$), 1032.9 ($[\mathbf{1}^{\mathbf{Zn}} - 3{\cdot}TfO^-]^{3+}$), 1046.6 ($[\mathbf{1}^{\mathbf{Zn}} + CH_3CN - 3{\cdot}TfO^-]^{3+}$), and 1623.9 ($[\mathbf{1}^{\mathbf{Zn}} - 2{\cdot}TfO^-]^{2+}$) (Fig. 2d). These results, when coupled

---

[a] *Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan. E-mail: yoshizawa.m.ac@m.titech.ac.jp; Fax: +81-45-924-5230; Tel: +81-45-924-5284*
[b] *Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima, Tokyo 196-8666, Japan*

† Electronic supplementary information (ESI) available: Experimental procedures, physical properties, and crystallographic data. CCDC 800615. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc12946e

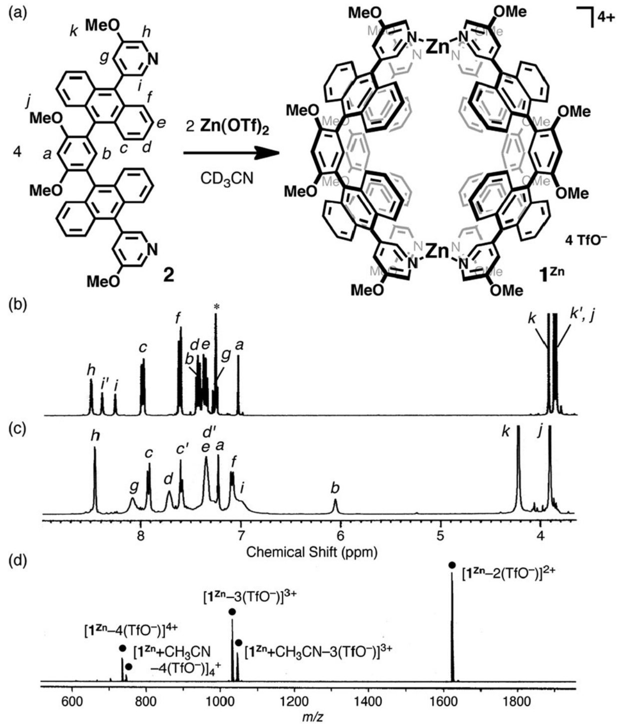

Fig. 2 (a) Schematic representation of the preparation of Zn(II)-linked molecular capsule $\mathbf{1^{Zn}}$ *via* self-assembly of bidentate ligand **2** and Zn(OTf)$_2$.[12,13] ^{1}H NMR spectra (400 MHz, rt) of (b) ligand **2** in CDCl$_3$ (*: CHCl$_3$) and (c) capsule $\mathbf{1^{Zn}}$ in CD$_3$CN. (d) ESI-TOF MS spectrum of a CH$_3$CN solution of $\mathbf{1^{Zn}}$.

with the lack of signals indicating $\mathbf{1^{Zn}}$ fragmentation, demonstrate the stability of the M$_2$L$_4$ capsule structure in high dilution under ESI-TOF MS conditions. Further ^{1}H NMR titration experiments corroborated the 2 : 4 metal to ligand ratio and revealed that no proton signals derived from intermediate species were observable during the self-assembly processes. The analogous M$_2$L$_4$ molecular capsules $\mathbf{1^{M}}$ where M = Ni or Pd[9] were prepared using similar procedures.[12]

X-ray crystallographic analysis firmly established the discrete, three-dimensional, hollow structure of the M$_2$L$_4$ molecular capsules. Pale yellow, X-ray quality single crystals of the Ni(II) analogue $\mathbf{1'^{Ni}}$ were obtained by slow vapor diffusion of CH$_3$OH into a CH$_3$CN solution of the capsule.[14] The distorted spherical structure of capsule $\mathbf{1'^{Ni}}$ possesses D_4-symmetry and is composed of four ligands and two Ni(II) ions (Fig. 3).[14] The coordination geometry of each Ni(II) atom is octahedral with the four pyridyl groups coordinated in the square planar position. The apical positions of one of the Ni atoms are occupied by one H$_2$O and one CH$_3$CN molecule, whereas two H$_2$O molecules occupy the apical positions of the other Ni atom. Both of the distance between the two Ni(II) atoms and that between the antipodal anthracene rings are ~13.5 Å. A single counter ion (ClO$_4^-$) and several CH$_3$OH molecules are incarcerated within the anthracene framework of $\mathbf{1'^{Ni}}$ (Fig. 3b and c). The optimized structure of $\mathbf{1^{Zn}}$ closely resembles the crystal structure of $\mathbf{1'^{Ni}}$ and, combined with the NMR and MS data, substantiates a spherical M$_2$L$_4$ capsule structure for $\mathbf{1^{Zn}}$ (Fig. S33, ESI†).[12,15]

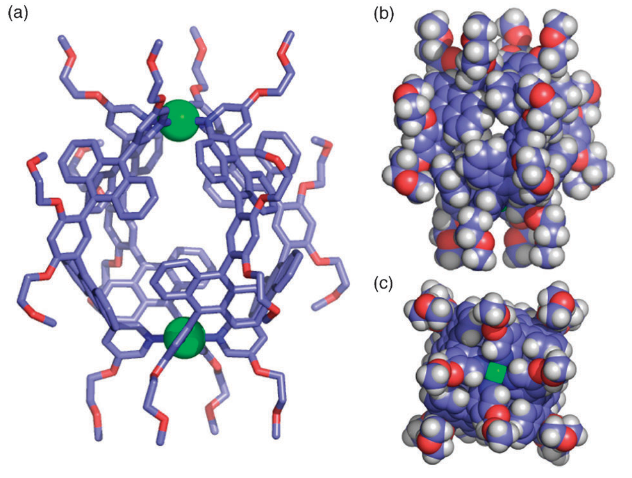

Fig. 3 X-ray crystal structure of Ni(II)-linked molecular capsule $\mathbf{1'^{Ni}}$: (a) a stick and ball representation without hydrogen atoms (Ni: green ball), and (b) side and (c) top views using a space-filling representation. The counterions and solvent molecules are omitted for clarity.

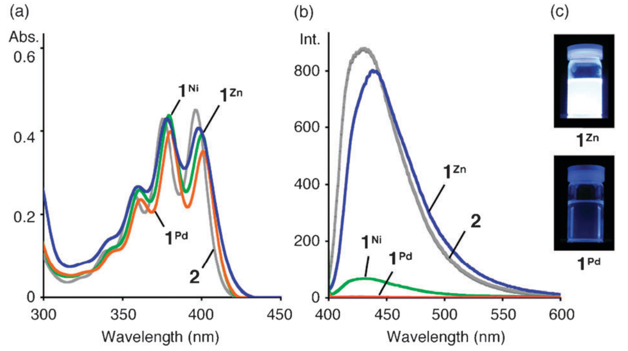

Fig. 4 (a) UV-vis (CH$_3$CN, $\mathbf{1^{M}}$: 0.056 mM, **2**: 0.23 mM, rt) and (b) fluorescence (degassed CH$_3$CN, λ_{ex} = 396 nm, rt) spectra of capsules $\mathbf{1^{Zn}}$ (blue line), $\mathbf{1^{Pd}}$ (orange line), $\mathbf{1^{Ni}}$ (green line) and ligand **2** (gray lines). (c) Blue emission from $\mathbf{1^{Zn}}$ and no emission of $\mathbf{1^{Pd}}$ in CH$_3$CN under UV irradiation (λ_{ex} = 365 nm) at rt.

The UV-vis spectra of molecular capsules $\mathbf{1^{M}}$ in CH$_3$CN are dominated by the π–π* transitions of the anthracene moieties from 320 to 430 nm (*e.g.*, $\mathbf{1^{Zn}}$: λ_{max} = 378 nm, ε = 75 × 10^3 M^{-1} cm^{-1}) (Fig. 4a). In ligand **2** and capsule $\mathbf{1^{M}}$, the anthracene rings are held orthogonal to the pyridine rings[16] so that the absorption bands in capsules $\mathbf{1^{M}}$ exhibit only a minor red shift ($\Delta\lambda \leq +5$ nm) with respect to ligand **2**.

Whereas the absorptive properties were insensitive to the identity of the metal hinge in capsules $\mathbf{1^{M}}$ (M = Zn, Ni, and Pd), the emissive properties turned out to be dependant on the transition metal ion. Irradiation of a degassed CH$_3$CN solution of Zn(II) capsule $\mathbf{1^{Zn}}$ at 396 nm resulted in blue emission at λ_{max} = 438 nm with an absolute quantum yield (Φ_F) of 0.81.[12] Ni(II) capsule $\mathbf{1^{Ni}}$ also exhibited similar emission (λ_{max} = 431 nm, Φ_F = 0.20) but capsule $\mathbf{1^{Pd}}$ was essentially non-emissive ($\Phi_F \approx 0.00$) (Fig. 4b and c).

The emission features and the quantum yield of $\mathbf{1^{Zn}}$ closely match that of the parent luminophore in ligand **2** (λ_{max} = 434 nm, Φ_F = 0.79) and indicate that each of the eight, closely assembled, anthracene rings of the capsule behaves as independent luminophores.[17] Switching from Zn(II) to Ni(II) results in slight quenching of the emission due to the presence of the paramagnetic metal ions, yet the emission maximum and shape remain almost unchanged. Emission from the Zn(II) capsule displayed greater oxygen sensitivity than free ligand **2**: in aerated solutions, emission from $\mathbf{1}^{\mathbf{Zn}}$ was quenched by 46% whereas that from **2** was only quenched by 19%.[18]

In summary, we have prepared metal-linked M_2L_4 molecular capsules with ~1 nm cavities fully enshrouded by the eight large panels of anthracene fluorophores. In sharp contrast to the majority of previous coordination cages and analogous Pd(II) capsules, the Zn(II) and Ni(II) capsules are emissive with the high and moderate quantum yields, respectively. The emissive properties of these new molecular capsules bearing fluorescent shells promise novel applications where supramolecular host–guest interactions can be used to develop new fluorescent functional materials, sensors, and devices. These novel fluorescent capsules are particularly attractive as zinc is a "green" transition metal and the exterior functional groups can be readily modified and elaborated.

This work was supported by the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) *via* Grants-in-Aid for Scientific Research on Innovative Areas "Coordination Programming" (Area 2107, No. 21108011) and the global COE program (GCOE) "Education and Research Center for Emergence of New Molecular Chemistry", and the Japan Society for the Promotion of Science (JSPS) *via* "Funding Program for Next Generation World-Leading Researchers". The authors would like to thank Dr. J. K. Klosterman for his helpful discussions.

Notes and references

1 (*a*) B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, 2002; (*b*) V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines: Concepts and Perspectives for the Nanoworld*, Wiley-VCH, Weinheim, 2nd edn, 2008.

2 (*a*) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515–1566; (*b*) L. Prodi, F. Bolletta, M. Montalti and N. Zaccheroni, *Coord. Chem. Rev.*, 2000, **205**, 59–83.

3 (*a*) B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022–2043; (*b*) S. R. Seidel and P. J. Stang, *Acc. Chem. Res.*, 2002, **35**, 972–983; (*c*) F. Hof, S. L. Craig, C. Nuckolls and J. Rebek, Jr., *Angew. Chem., Int. Ed.*, 2002, **41**, 1488–1508; (*d*) D. Fiedler, D. H. Leung, R. G. Bergman and K. N. Raymond, *Acc. Chem. Res.*, 2005, **38**, 349–358; (*e*) M. Fujita, M. Tominaga, A. Hori and B. Therrien, *Acc. Chem. Res.*, 2005, **38**, 369–378; (*f*) J. Rebek, Jr., *Angew. Chem., Int. Ed.*, 2005, **44**, 2068–2078; (*g*) J. K. Klosterman, Y. Yamauchi and M. Fujita, *Chem. Soc. Rev.*, 2009, **38**, 1714–1725; (*h*) M. Yoshizawa, J. K. Klosterman and M. Fujita, *Angew. Chem., Int. Ed.*, 2009, **48**, 3418–3438.

4 (*a*) N. K. Al-Rasbi, C. Sabatini, F. Barigelletti and M. D. Ward, *Dalton Trans.*, 2006, 4769–4772; (*b*) K. Harano, S. Hiraoka and M. Shionoya, *J. Am. Chem. Soc.*, 2007, **129**, 5300–5301; (*c*) I. S. Tidmarsh, T. B. Faust, H. Adams, L. P. Harding, L. Russo, W. Clegg and M. D. Ward, *J. Am. Chem. Soc.*, 2008, **130**, 15167–15175.

5 There are a few exceptions where Pt(II)-linked coordination cages show strong emission from the large aromatic subunits: (*a*) M. Busi, M. Laurenti, G. G. Condorelli, A. Motta, M. Favazza, I. L. Fragala, M. Montalti, L. Prodi and E. Dalcanale, *Chem.–Eur. J.*, 2007, **13**, 6891–6898; (*b*) S. Ghosh and P. S. Mukherjee, *Organometallics*, 2008, **27**, 316–319.

6 (*a*) M. Kessinger and J. Michl, *Excited States and Photochemistry of Organic Molecules*, VCH, New York, 1995; (*b*) N. J. Turro, *Modern Molecular Photochemistry*, Benjamin, Menlo Park, 1978.

7 (*a*) S. Yamaguchi, S. Akiyama and K. Tamao, *J. Am. Chem. Soc.*, 2001, **123**, 11372–11375; (*b*) K. Suzuki, A. Seno, H. Tanabe and K. Ueno, *Synth. Met.*, 2004, **143**, 89–96; (*c*) A. Petitjean, R. G. Khoury, N. Kyritsakas and J.-M. Lehn, *J. Am. Chem. Soc.*, 2004, **126**, 6637–6647; (*d*) W. J. Yang, D. Y. Kim, M.-Y. Jeong, H. M. Kim, Y. K. Lee, X. Fang, S.-J. Jeon and B. R. Cho, *Chem.–Eur. J.*, 2005, **11**, 4191–4198; (*e*) Y. H. Kim, H. C. Jeong, S. H. Kim, K. Yang and S. K. Kwon, *Adv. Funct. Mater.*, 2005, **15**, 1799–1805.

8 (*a*) M. Scherer, D. L. Caulder, D. W. Johnson and K. N. Raymond, *Angew. Chem., Int. Ed.*, 1999, **38**, 1588–1592; (*b*) M. R. Johnston, M. J. Latter and R. N. Warrener, *Org. Lett.*, 2002, **4**, 2165–2168; (*c*) W. Meng, B. Breiner, K. Rissanen, J. D. Thoburn, J. K. Clegg and J. R. Nitschke, *Angew. Chem., Int. Ed.*, 2011, **50**, 3479–3483.

9 N. Kishi, Z. Li, K. Yoza, M. Akita and M. Yoshizawa, submitted.

10 M_2L_4 coordination cages with Pd(II) ions: (*a*) D. A. McMorran and P. J. Steel, *Angew. Chem., Int. Ed.*, 1998, **37**, 3295–3297; (*b*) D. K. Chand, K. Biradha and M. Fujita, *Chem. Commun.*, 2001, 1652–1653; (*c*) N. L. S. Yue, D. J. Eisler, M. C. Jennings and R. J. Puddephatt, *Inorg. Chem.*, 2004, **43**, 7671–7681; (*d*) G. H. Clever, S. Tashiro and M. Shionoya, *Angew. Chem., Int. Ed.*, 2009, **48**, 7010–7012; (*e*) P. Liao, B. W. Langloss, A. M. Johnson, E. R. Knudsen, F. S. Tham, R. R. Julian and R. J. Hooley, *Chem. Commun.*, 2010, **46**, 4932–4934.

11 Ligand **2** was synthesized in six steps from 1,3-dimethoxybenzene using Negishi and Suzuki–Miyaura palladium catalyzed cross-coupling procedures (48% total yield).[12] The pyridyl methoxy groups of **2** serve as useful NMR tags to monitor the capsule formation, as they are quite sensitive to metal coordination.

12 See ESI.† The Ni(II) capsule exhibited paramagnetic behavior as is evident from its ^1H NMR spectra. Instead, the M_2L_4 composition of the capsule was determined by ESI-TOF MS analysis.

13 Axial ligands (L′) coordinated to the Zn(II) center (L′ = CD_3CN, TfO^-, and/or H_2O) are omitted for clarity.

14 The methoxy groups of $\mathbf{1}^{\mathbf{Ni}}$ were replaced with methoxyethoxy groups in $\mathbf{1'}^{\mathbf{Ni}}$ to facilitate crystallization. X-Ray crystal data of $\mathbf{1'}^{\mathbf{Ni}}$: $C_{234}H_{249}Cl_4N_9Ni_2O_{59}$, $M_r = 4390.78$, crystal dimensions $0.15 \times 0.11 \times 0.10$ mm^3, tetragonal, $P4nc$, $a = b = 19.4133(4)$ Å, $c = 29.968(2)$ Å, $V = 11294.4(9)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.291$ g cm^{-3}, F(000) = 4624, radiation, $\lambda(\text{Cu}K\alpha) = 1.54187$ Å, $T = 93(2)$ K, reflections collected/unique 124 070/10 352 ($R_{\text{int}} = 0.0448$). The structure was solved by the direct methods (SIR2004) and refined by full-matrix least-squares methods on F^2 with 745 parameters. $R_1 = 0.0573$ ($I > 2\sigma(I)$), $wR_2 = 0.1606$, GOF 0.981; max/min residual density 0.592/−0.603 eÅ^{-3}. CCDC 800615.

15 Octahedral coordination geometry of Zn(II)-complexes: (*a*) P. Losier and M. J. Zaworotko, *J. Chem. Crystallogr.*, 1996, **26**, 277–280; (*b*) D. R. Turner, M. Henry, C. Wilkinson, G. J. McIntyre, S. A. Mason, A. E. Goeta and J. W. Steed, *J. Am. Chem. Soc.*, 2005, **127**, 11063–11074; (*c*) T. D. Hamilton, D.-K. Bucar, M. B. J. Atkinson, G. S. Papaefstathiou and L. R. MacGillivray, *J. Mol. Struct.*, 2006, **796**, 58–62.

16 J. Iwasa, K. Ono, M. Fujita, M. Akita and M. Yoshizawa, *Chem. Commun.*, 2009, 5746–5748.

17 The emission capability of capsule $\mathbf{1'}^{\mathbf{Zn}}$ bearing methoxyethoxy groups was similar to that of $\mathbf{1}^{\mathbf{Zn}}$.

18 The emission lifetime (τ) of $\mathbf{1}^{\mathbf{Zn}}$ (12 ns) is longer than that of **2** (10 ns). In the solid state, an emission spectrum ($\lambda_{\text{ex}} = 396$ nm) of capsule $\mathbf{1}^{\mathbf{Zn}}$ showed a broadened band ($\lambda_{\max} = 460$ nm) with an absolute quantum yield (Φ_F) of 0.06.