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A Highly Fluorescent Anthracene-Containing Hybrid Material Exhibiting Tunable Blue–Green Emission Based on the Formation of an Unusual "T-Shaped" Excimer

Guoqi Zhang,[a] Guoqiang Yang,*[a] Shuangqing Wang,[a] Qingqi Chen,[b] and Jin Shi Ma*[a]

Abstract: A series of flexible bis(9-anthryldiamine) ligands (**L1**–**L3**) linked with alkyl spacers of different chain length was synthesized and characterized, in order to investigate the coordination behavior of these diamine ligands with metal ions (Zn^{2+}, etc.) based on fluorescence measurements. The results showed that, in the case of anthryldiamine ligands bearing two- or four-carbon links, the zinc ion induced a chelation-enhanced fluorescence (CHEF) effect in aqueous media, while a trace amount of water could selectively quench the blue emission of the Zn^{II} complex with a three-carbon-linked ligand (**1**). Meanwhile, the introduction of more water (concentration >11%) resulted in the formation of a new green luminescent species; the luminescence intensity was enhanced stepwise to a maximum with addition of approximately 30% water in THF solution. The peak position (centered at approximately 500 nm) and the lifetime measurement ($\tau = 19.59$ ns) indicated that the green luminescence was attributable to a novel edge-to-face dimeric conformation ("T-shaped" conformation) of anthracene, and not to the more common face-to-face dimeric conformation. Accordingly, ^1H NMR spectroscopic studies in nonaqueous or aqueous solution confirmed this T-shaped conformation, which is consistent with the results of single-crystal X-ray structure analysis and solid-state photoluminescence studies.

Keywords: anthracene · excimers · fluorescence · sensors · water chemistry

Introduction

Luminescent inorganic–organic hybrid compounds are an important class of molecules that have extensive applications in biology, chemistry, and materials science. Anthracene derivatives are key species in the design of luminescent supramolecular materials, which have found wide utilization in lasers, phosphors, and light-emitting devices.[1] Although a tremendous number of anthracene-based organic materials have been investigated with the aim of potential applications as photoluminescence (PL) and/or electroluminescence (EL) devices in films and the solid state, the practical development of PL and EL devices is in fact restricted, usually owing to their poor stability. In contrast, strongly luminescent anthracene-based inorganic–organic hybrid materials with higher stability could be a class of promising candidates for light-emitting as well as EL applications.[2]

On the other hand, anthrylpolyamine chemosensors have been widely researched in pH switching, the detection of alkali-metal, alkaline-earth, and heavy-metal cations, or even the recognition of various anions.[2,3] In particular, Czarnik and co-workers reported their pioneering work on the investigation of anthrylpolyamine fluorescent chemosensors for metal-ion recognition about two decades ago.[3a–c] Originally, they reported the dramatic fluorescence enhancement (up to 1000-fold) of 9,10-disubstituted anthrylpolyamine derivatives induced by zinc chloride in organic solvent, and demonstrated a remarkable chelation-enhanced fluorescence (CHEF) effect on these systems, indicating the

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[a] Dr. G. Zhang, Prof. G. Yang, S. Wang, J. S. Ma
Beijing National Laboratory for Molecular Sciences
CAS Key Laboratory of Photochemistry
Institute of Chemistry, Chinese Academy of Sciences
Beijing 100080 (China)
Fax: (+86) 10-8261-7315
E-mail: gqyang@iccas.ac.cn
jsma@iccas.ac.cn

[b] Dr. Q. Chen
Biomarin Pharmaceutical, Inc.
46 Galli Drive, Novato, CA 94949 (USA)

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great potential of this type of organic compound as a technically facile fluorescent analytical probe.[3b]

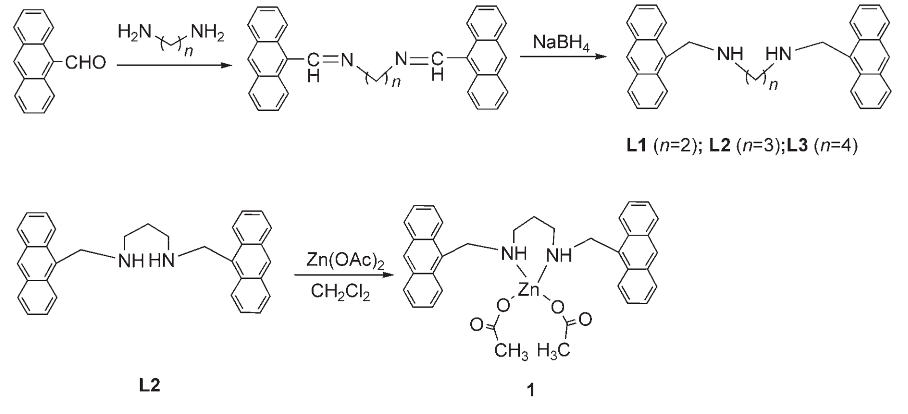
In recent years, many luminescent inorganic–organic hybrids were found to efficiently detect neutral small molecules, such as acetonitrile, ethanol, benzene, and toluene,[2] which are of environmental importance. Despite the number of reports on anthrylpolyamine systems as promising fluorescent host compounds for guest recognition,[3,4] no water-recognition anthrylpolyamine–metal hybrid was observed, as almost all of them usually operate in hydrous media. Nevertheless, previous work has confirmed that water could to some degree influence the complexation of metal ions to an anthrylpolyamine host.[3b]

Herein, we present the first example of a highly fluorescent anthrylpolyamine–zinc(II) hybrid material which displays novel water-tunable blue–green light emission upon UV irradiation both in solution and in the solid state. Interestingly, we found that this complex was extremely sensitive towards water in organic solution at a very low range of concentration, but upon addition of a much larger amount of water (over approximately 11%) a new green-light-emitting species formed, which was clearly different from the behaviors of previously reported anthrylpolyamine derivatives. Most excitingly, for the first time we observed directly the formation of a "T-shaped" anthracene–anthracene dimer both in solution and in the solid state, on the basis of detailed spectroscopic, photophysical studies and X-ray structure analysis.

Results and Discussion

The anthryldiamine ligands **L1**–**L3** were efficiently synthesized by condensation of 9-anthracylaldehyde and appropriate diamines, followed by in situ reduction with excess $NaBH_4$ (Scheme 1). Ligands **L1**–**L3** were found to be very weakly emissive due to the well-known photoinduced electron transfer (PET) fluorescence quenching process.[5] To investigate the coordination properties of these diamine ligands with metal ions, we attempted to detect their fluorescent response to various metal ions. Accordingly, the zinc ion remarkably results in the CHEF effect, similar to the observed behavior of Czarnik's anthrylpolyamine systems and other reported polyamine donors.[3a,b,6] Indeed, both **L1** and **L3** displayed strongly selective fluorescence enhancement upon introduction of Zn^{2+} in hydrous media (see Supporting Information). But addition of Zn^{2+} to **L2** resulted in no obvious emission enhancement of anthracene monomer in the presence of water, despite the increased emission in anhydrous organic solvent.

A strongly fluorescent complex **1** was obtained in high yield by reacting **L2** with zinc acetate in CH_2Cl_2/MeOH (1:1 v/v) at room temperature (Scheme 1). Complex **1** exhibits the characteristic absorption of anthracene in the range of 320–380 nm, and shows strong blue luminescence both in water-free solution and in the solid state on irradiation with UV light. In common organic solvents, such as toluene, dichloromethane, THF, methanol, and ethanol, the quantum efficiency of **1** is rather high ($\Phi_f = 0.47$ in THF, relative to that of 9,10-diphenylanthracene,[7] and $\tau = 5.54$ ns). However, in solvents which contain a trace amount of water, the quantum yield decreases dramatically. To elucidate the water-mediated fluorescence-quenching effect, a fluorescence spectrometric titration experiment was carried out sequentially. Figure 1a shows clearly the expected quenching effect. Upon increasing the water content from 1 to 9 μL in a solution of **1** in dry THF (3 mL, concentration $c = 5$ μM), the emission gradually decreased, and the quantum efficiency fell to 0.08 when 5 μL of water was added. This was probably because a small amount of water would interact partially with zinc centers to release zinc ions from the amino group of the ligands.[3b] Consequently, this resulted in the PET process in the excited state and quenched the emission of the anthracene monomer. This remarkable fluorescence quenching property induced by a trace amount of water was very interesting, and extremely rare examples exhibiting water-recognition ability by fluorescence changes have been reported.[8] Thus, compound **1** might have a potential application as a fluorescent sensor for detecting trace amounts of water.



Scheme 1.

It was further noted that when the water concentration in THF was below 11%, the quenched emission of **1** was not significantly changed. However, when the water concentration was higher than 11%, the emission changed dramatically and a new emission band appeared at approximately 500 nm (Figure 1b). The water-tuning emission of **1** was illustrated clearly by the evolution of the fluorescence spectra with changing water concentration, and the corresponding photograph was taken under a UV lamp (Figure 2). It can be clearly seen that the color of the emission in solution evolves from

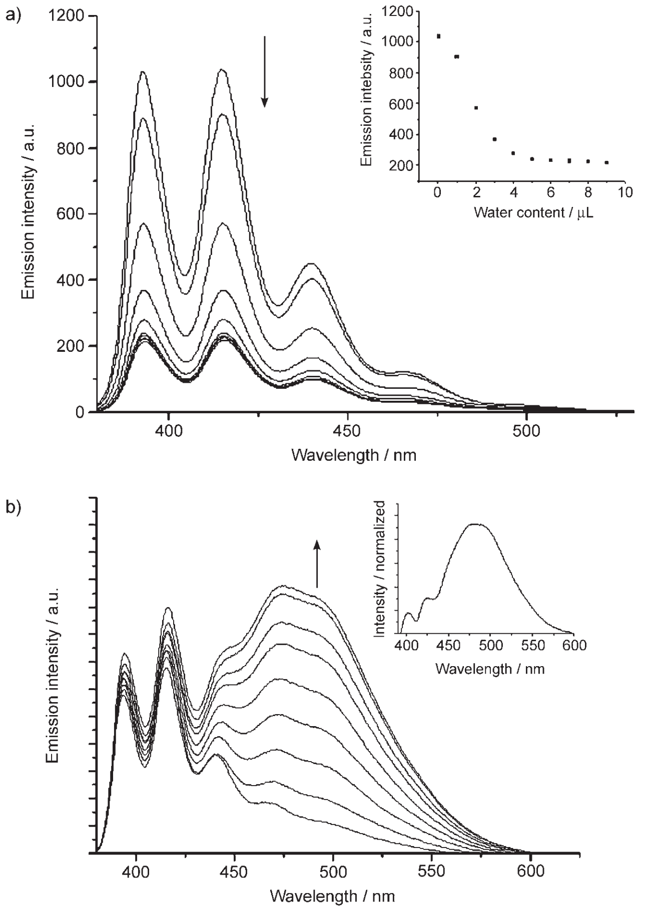


Figure 1. a) Water-driven fluorescence quenching of **1** ($c=5\times10^{-6}$ M) in THF (3 mL); water was added in amounts of 0, 1, 2, 3, 4, 5, 6, 7, 8, and 9 µL, respectively. Inset: Plot of emission intensity versus quantity of added water in THF at 415 nm; $\lambda_{ex}=368$ nm. b) Water-induced emission changes of **1** ($c=5$ µM) in THF/H$_2$O (from 9:1 to 3:1 v/v); $\lambda_{ex}=368$ nm. Inset: Fluorescence differential spectrum of **1** from those in THF and H$_2$O/THF (1:3 v/v).

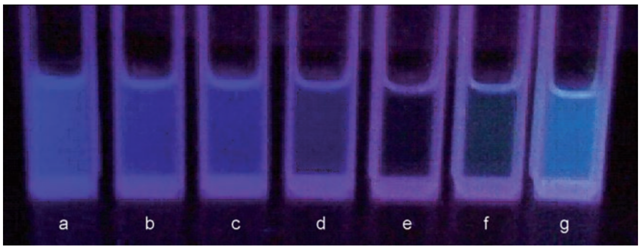


Figure 2. Photographs of fluorescence emission from the solution of **1** in THF/H$_2$O with changing water concentration (a–g: 0, 0.05, 0.1, 0.2, 5, 15, and 30%, respectively) under a UV lamp. The concentration of the solutions was kept at 5×10^{-6} M.

blue to green with increasing water content. Such a blue–green emission change could also be observed when the THF or THF/H$_2$O solutions of **1** were deposited on glass surfaces as a thin film by the spin-coating method (see Supporting Information). The dramatic spectral changes induced by water could be attributed to the formation of aggregates in solution. As **1** was insoluble in water, it was very likely that molecules of **1** would tend to slightly aggregate in the H$_2$O/THF mixture when the water concentration was increased, as most of the organic molecules did.[9] In order to reveal the quantitative relationship between the new green luminescence intensity and the water concentration in THF solution, we plotted the changes in peak area of the green luminescence around 500 nm with the increase of water concentration (see Supporting Information). The plot clearly showed a sequential increase of the peak area of the green luminescence with increasing water concentration in the range of 11–30%, indicative of the quantitative formation of a new emissive species. Compared to the most common anthracene-related compounds, which formed a face-to-face dimeric conformation in solution and usually displayed an emission band at 530–550 nm,[10] the emission band of **1** was blue-shifted by approximately 30 nm. This finding suggested that in solution, **1** did not adopt a face-to-face π-stacked dimeric conformation but an edge-to-face dimeric conformation (T-shaped conformation), which was further indicated by measurement of the lifetime of this species ($\tau=19.59$ ns), remarkably different from the π-stacked dimer with a longer lifetime (>200 ns).[11] Furthermore, this was also confirmed by the ^{1}H NMR spectra in solution.

^{1}H NMR spectroscopic studies are helpful for the investigation of the aggregation interactions of **1** with the T-shaped conformation in solution. Figure 3 displays the results of ^{1}H NMR spectral change in the low-field region before (A) and after (B) water (D$_2$O) was added to the [D$_8$]THF solution. The most remarkable change came from the strong upfield shift of one edge-ring proton (H$_d$) of the anthryl group, which indicated that this proton was located in the shielding area of the aromatic ring and was strongly shielded by the "ring current" in hydrous solution. This result supports the formation of a T-shaped anthracene–anthracene dimer in the new aggregate structure upon addition of water.

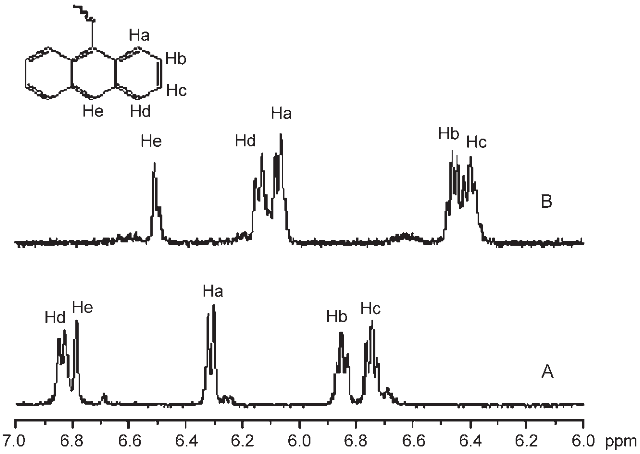


Figure 3. Partial ^{1}H NMR spectra of **1** in A) [D$_8$]THF and B) [D$_8$]THF/D$_2$O (70:30 v/v).

Single crystals of **1** were obtained by slow evaporation of toluene/ether solution. Careful diffusion of ether to CH$_2$Cl$_2$, THF, or THF/H_2O (5:1 v/v) solutions of **1** gave blocklike crystals **1a–c**, respectively. Interestingly, although they contained the same molecular composition, the emission properties of the crystals were different. Crystals of **1a** and **1b** emit blue light, whereas those of **1c** emit green light upon UV irradiation (Figure 4 and Supporting Information). Crystals **1a** and **1b** display nearly the same emission spectra with a structureless monomer emission at 448 nm. Crystals of **1c**, however, show an intense fluorescence emission at $\lambda_{max}=$ 500 nm. This remarkable red-shifted emission band is apparently not from a monomer excited state, in contrast to common anthracene derivatives.[4] Furthermore, the luminescence of the ground and vacuum-dried powdered crystals of **1c** retained the green-emitting feature, and crystals of **1a** and **1b** did not change their emission color on exposure to air for a long time (>10 days). Thus, the possibility of a solvent-incorporated luminescence change was excluded, in contrast to other reported solvent-sensitivity luminescent complexes,[4] but a T-shaped excited-state dimer (excimer) induced by water during crystallization should be responsible for the green photoluminescence of **1c**, which was also reminiscent of the emission and the ^{1}H NMR spectral changes of **1** in H_2O/THF solution depicted in Figure 3.

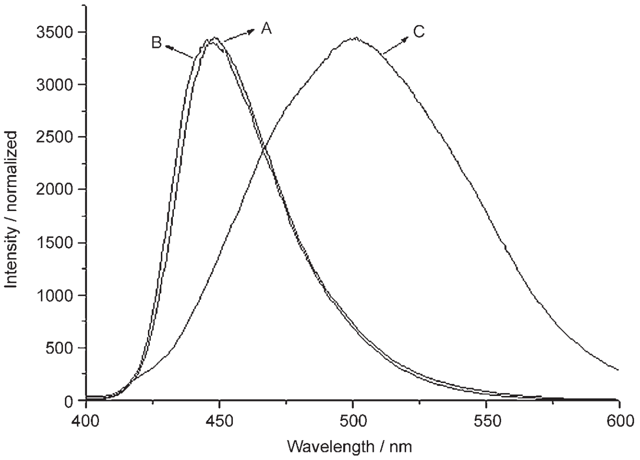


Figure 4. Solid-state photoluminescence spectra for ground crystals of **1a–c** at ambient temperature. (A: **1a**, B: **1b**, C: **1c**; $\lambda_{ex}=368$ nm).

As crystals of **1a** and **1b** displayed the same characteristic, only good-quality single crystals of **1a** were collected for X-ray structure analysis. The results of the X-ray structure analysis of **L2**, **1a**, and **1c** are shown in Figure 5. The free ligand **L2** crystallizes in an orthorhombic system and adopts a rather interesting dimeric structure with N−H···N hydrogen bonds (H···N = 2.616 Å, N···N = 3.182 Å, and N-H-N = 121.7°).

Crystals **1a** and **1c** adopted different crystallization patterns though both were from the same material. While **1a** crystallized in the triclinic space group $P\bar{1}$, **1c** crystallized in the monoclinic space group *Cc*. In the crystal lattice of **1a**, very weak face-to-face π···π and edge-to-face C−H···π-ring center interactions were observed. The closest centroid–centroid distance and H···π-ring center distance between anthracene rings are 374.0 and 345.2 pm, respectively

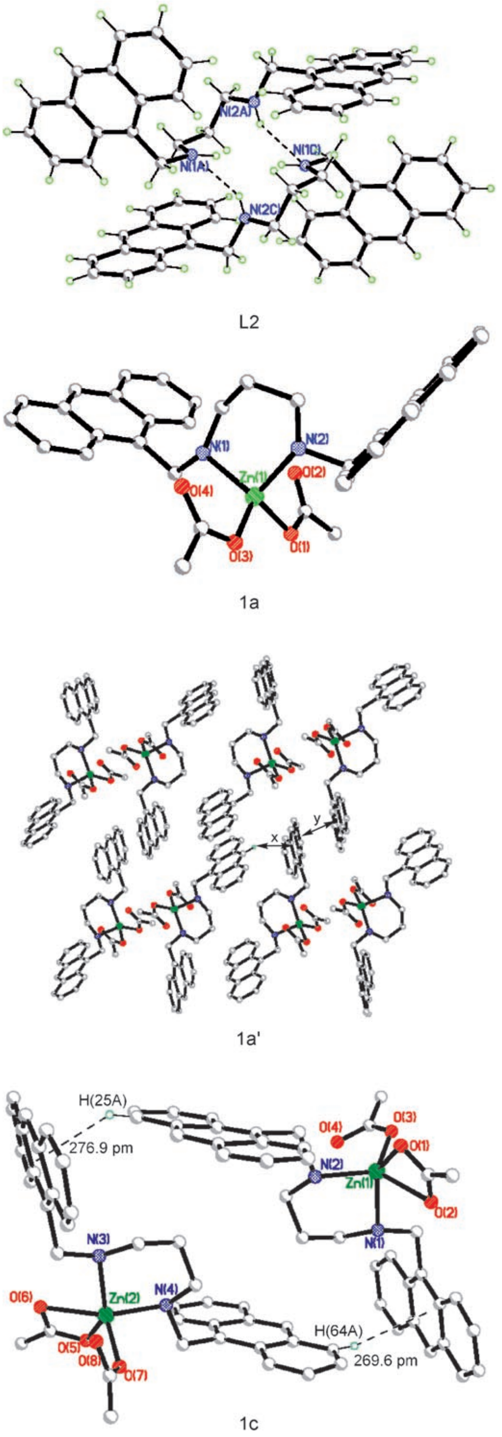


Figure 5. X-ray crystal structures of **L2**, **1a**, and **1c**. The packing diagram of **1a** is depicted as **1a'**, in which $x=345.2$ pm, $y=374.0$ pm. Green sphere: zinc; green ring: hydrogen; gray: carbon; blue: nitrogen; red: oxygen. Selected data for **1a**: Zn1−O1 1.930(3), Zn1−O3 1.948(3), Zn1−N1 2.034(4), Zn1−N2 2.071(3) Å; O1-Zn1-O3 103.99(15), O1-Zn1-N1 123.65(14), O3-Zn1-N1 114.31(14), O1-Zn1-N2 110.47(14), O3-Zn1-N2 102.37(14), N1-Zn1-N2 100.14(12)°; for **1c**: Zn1−O3 1.851(10), Zn1−N2 2.046(9), Zn1−N1 2.114(10), Zn1−O1 2.159(10), Zn1−O2 2.324(13) Å; O3-Zn1-N2 121.0(5), O3-Zn1-N1 109.8(4), N2-Zn1-N1 95.9(4), O3-Zn1-O1 103.9(4), N2-Zn1-O1 92.4(4), N1-Zn1-O1 134.2(4), O3-Zn1-O2 117.9(6), N2-Zn1-O2 117.7(5), N1-Zn1-O2 81.9(4), O1-Zn1-O2 54.8(4)°.

(Figure 5). Apparently, these weak packing interactions stabilized the crystalline material but the distance was not short enough to result in the "excimer" emission. Significantly, in the crystal lattice of **1c**, two isostructural molecules are mutually close, and therein the shortest intermolecular distances of 269.6 and 276.9 pm were observed between one anthracene center and one edge-ring hydrogen atom from another molecule. Two adjacent anthracene-ring planes are of an almost orthogonal arrangement (77.0 and 71.3°), thus forming a well-defined T-shaped geometry, which was apparently responsible for the green light emission under UV irradiation. The crystallographic analysis data are also well consistent with the results of ^{1}H NMR spectroscopic studies in solution. Furthermore, this provides the first observation of an anthracene–anthracene T-shaped C−H⋅⋅⋅π interaction which led to an excimer emission.[12] There are only a few examples of T-shaped C−H⋅⋅⋅π interactions observed in excited complexes, such as toluene–benzene[13] and toluene–anthracene.[4,14]

Conclusion

A chain-length-selective approach to water-induced emission change based on a highly fluorescent inorganic–organic hybrid material has been studied and established. The remarkable change of emission characteristic tuned by different amounts of water may be regarded as a special type of chemosensing. Significantly, such dramatic water-induced on–off switching of emission, and sensitive change in the emission color of crystals by aggregation of polyaromatic hydrocarbon and formation of a T-shaped excimer, has not been previously reported. The complex would perform as a versatile candidate for chemosensors and probes of environmental changes, and has promising applications in photofunctional materials as well.

Experimental Section

General: Ligand **L1** was synthesized by a previously described method.[3c] All other reagents were commercially available and used without further purification. Solvents for syntheses were purified according to standard methods, while for spectra measurement they were purchased as spectrophotometric grade. Samples for C, H, and N analyses were dried under vacuum and the analyses were performed with a Carlo Erba 1106 instrument. ^{1}H NMR and ^{13}C NMR spectra were measured with a Bruker dmx 300 or 400 MHz NMR spectrometer at room temperature. The ESI and MALDI-TOF mass spectrometry (MS) measurements were carried out with a Bruker APEX II instrument. UV/visible absorption spectra were obtained on a Hitachi UV-3010 absorption spectrophotometer. Steady-state excitation and emission spectra were recorded on a Hitachi F-2500 fluorescence spectrophotometer. The fluorescence lifetime was obtained from a Lifespec-ps fluorescence lifetime analytical spectrometer (Edinburgh Instruments).

N,N′-Bis(anthracen-9-ylmethyl)propane-1,3-diamine (L2): 9-Anthracylaldehyde (4.7 g, 24 mmol) was dissolved in CH_2Cl_2/MeOH (60 mL; 1:2 v/v) and then heated at reflux under N_2. A solution of 1,3-diaminopropane (0.8 mL, 12 mmol) dissolved in CH_3OH (10 mL) was subsequently added dropwise with rigorous stirring. The mixture was refluxed for 4 h and the yellow solution was cooled to 50 °C. An excess of $NaBH_4$ (5.2 g) dissolved in CH_3OH (15 mL) was added in small portions over 2 h. The mixture turned increasingly to a clear yellowish color and the resulting solution was reacted at room temperature overnight. The solvent was removed under reduced pressure, and the residue was treated with excess water. The undissolved solid was collected by filtration, then recrystallized twice from toluene/ether to give light yellow blocks. Yield: 3.5 g, 65 %; m.p. 109–111 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.62$ (br s, 2H; NH), 1.86 (m, 2H; CH_2), 2.96 (t, $J = 6.75$ Hz, 4H; CH_2), 4.69 (s, 4H; CH_2), 7.44 (m, 8H; anthryl-H), 7.96 (d, $J = 8.0$ Hz, 4H; anthryl-H), 8.28 (d, $J = 9.0$ Hz, 4H; anthryl-H), 8.37 ppm (s, 2H; anthryl-H); EIMS: m/z: 454 $[M]^+$; elemental analysis calcd (%) for $C_{33}H_{31}N_2 \cdot 1/2\,H_2O$: C 85.49, H 6.74, N 6.04; found: C 85.05, H 7.19, N 6.18.

N,N′-Bis(anthracen-9-ylmethyl)butane-1,4-diamine (L3): 9-Anthracylaldehyde (4.7 g, 24 mmol) was dissolved in CH_2Cl_2/MeOH (60 mL; 1:2 v/v) and then heated at reflux under N_2. A solution of 1,4-diaminobutane (0.8 mL, 12 mmol) dissolved in CH_3OH (10 mL) was subsequently added dropwise with rigorous stirring. The mixture was refluxed for 4 h and the yellow solution was cooled to 50 °C. An excess of $NaBH_4$ (5.0 g) dissolved in CH_3OH (18 mL) was added in small portions over 2 h. The mixture turned increasingly to a clear yellowish color and the resulting solution was reacted at room temperature overnight. The solvent was removed under reduced pressure, and the residue was treated with excess water. The undissolved solid was collected by filtration, then recrystallized twice from toluene/ether to give pale-yellow blocks. Yield: 3.9 g, 70 %; m.p. 116–117 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.52$ (br s, 2H; NH), 1.68 (br s, 4H; CH_2), 2.88 (br s, 4H; CH_2), 4.69 (s, 4H; CH_2), 7.47 (m, 8H; anthryl-H), 7.99 (d, $J = 8.1$ Hz, 4H; anthryl-H), 8.30 (d, $J = 8.6$ Hz, 4H; anthryl-H), 8.39 ppm (s, 2H; anthryl-H); EIMS: m/z: 468 $[M]^+$; elemental analysis calcd (%) for $C_{34}H_{32}N_2$: C 87.14, H 6.88, N 5.98; found: C 87.29, H 6.95, N 5.96.

Complex 1: A solution of **L2** (454 mg, 1 mmol) in CH_2Cl_2 (5 mL) was added to a solution of $Zn(OAc)_2 \cdot 2\,H_2O$ (219 mg, 1 mmol) in CH_3OH (5 mL) at ambient temperature. The solution was stirred for 30 min and a gray precipitate appeared; stirring was continued overnight and the gray powder was collected by suction filtration. The crude product was recrystallized from THF to give **1** as yellowish blocks. Yield: 522 mg, 82 %; m.p. 220–221 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.70$ (br s, 2H; NH), 2.16 (s, 6H; CH_3COO), 2.66 (m, 2H; CH_2), 3.27 (m, 2H; CH_2), 3.61 (m, 2H; CH_2), 4.97 (m, 2H; CH_2), 5.16 (m, 2H; CH_2), 7.49 (t, $J = 8.0$ Hz, 4H; anthryl-H), 7.59 (t, $J = 8.3$ Hz, 4H; anthryl-H), 8.03 (d, $J = 8.4$ Hz, 4H; anthryl-H), 8.28 (d, $J = 8.8$ Hz, 4H; anthryl-H), 8.48 ppm (s, 2H; anthryl-H); EIMS: m/z: 577.3 $[\mathbf{1}-\mathrm{AcO}]^+$; elemental analysis calcd (%) for $C_{37}H_{36}N_2O_4Zn \cdot 1/2\,H_2O \cdot 1/2\,THF$: C 68.57, H 6.05, N 4.10; found: C 68.43, H 5.94, N 4.18.

X-ray crystallography: Accurate unit-cell parameters were determined by a least-squares fit of 2θ values, measured for 200 strong reflections, and intensity data sets were measured on a Rigarku Raxis Rapid IP diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at room temperature. The intensities were corrected for Lorentz and polarization effects, but no corrections for extinction were made. All structures were solved by direct methods. The non-hydrogen atoms were located in successive difference Fourier synthesis. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were added theoretically and riding on the concerned atoms. The crystallographic data and experimental details of the structure analyses are summarized in Table 1. CCDC-239341–239343 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.

Acknowledgements

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Table 1. Crystal and structure refinement data for compounds **L2, 1a**, and **1c**.

	L2	**1a** [Zn(**L2**)(OAc)$_2$·CH$_2$Cl$_2$]	**1c** [Zn$_2$(**L2**)$_2$(OAc)$_4$·THF·2H$_2$O]
empirical formula	$C_{33}H_{30}N_2$	$C_{38}H_{38}N_2O_4Cl_2Zn$	$C_{78}H_{79}N_4O_{11}Zn_2$
F_w	454.59	722.97	1379.2
crystal size [mm]	0.56 × 0.38 × 0.38	0.20 × 0.18 × 0.14	0.80 × 0.30 × 0.13
crystal color	pale yellow	light yellow	light yellow
crystal system	orthorhombic	triclinic	monoclinic
space group	*Pccn*	$P\bar{1}$	*Cc*
T [K]	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
a [Å]	23.126(5)	10.634(10)	11.679(2)
b [Å]	25.447(5)	11.913(12)	23.864(5)
c [Å]	8.3713(17)	14.390(14)	26.163(5)
α [°]	90.00	85.391(16)	90.00
β [°]	90.00	69.895(15)	97.57(3)
γ [°]	90.00	86.052(16)	90.00
V [Å^3]	4926.4(17)	1705(3)	7229(2)
Z	8	2	4
$F(000)$	1936	752	2892
ρ_{calcd} [g cm^{-3}]	1.226	1.408	1.267
μ [mm^{-1}]	0.071	0.921	0.725
reflections collected	5501	5987	8144
unique reflections	2883	4090	3598
variables	317	426	829
$R1$,[a] $wR2$[b] [%]	4.94, 14.54	5.55, 14.64	7.95, 21.71
Gof	1.058	1.065	0.946

[a] $R=(F_o-F_C)/(F_o)$. [b] $R_w=[w(F_o^2-F_c^2)^2/w(F_o^2)^2]^{1/2}$.

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