A Zinc(II) Complex Composed of a Tridentate Ligand Bearing Podand Pyrenyl Moieties

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The structural characterization and function of Zn^{II} complexes composed of a tridentate ligand bearing podand pyrenyl moieties as a fluorophore [2,6-pyridinedicarboxaldehydebis(1-pyrenylmethylimine) (L^1)] are described. The tridentate podand ligand L^1 forms a 2:1 complex, $[Zn(L^1)_2(BF_4)_2]$, with $Zn(BF_4)_2$ although the 1:1 complex $[Zn(L^1)(OAc)_2]$ is obtained with $Zn(OAc)_2$. The X-ray crystal structure determination of $[Zn(L^1)_2(BF_4)_2]$ reveals that two tridentate podand ligands L^1 coordinate meridionally to Zn^{II} ion to give an orthogonally oriented molecular turn around the approximately octahedral Zn^{II} center. One pyridyl moiety of L^1 is sandwiched in between two podand pyrenyl moieties of another L^1 through π-π interactions, together with an extended π-stacking through π-π interactions between the pyrenyl moieties in the crystal packing. $[Zn(L^1)(OAc)_2]$ serves as a fluorophore metalloreceptor possessing a two-guest binding ability. $[Zn(L^1)(OAc)_2]$ affords the 1:2 complex $[Zn(L^1)(G^1)_2]$ (G = guest molecule) with 4-nitrobenzoate ion (G^1). The X-ray crystal structure of $[Zn(L^1)(G^1)_2]$ confirms that $Zn(L^1)^{2+}$ accommodates two 4-nitrobenzoate moieties and that the coordination geometry around Zn^{II} is a distorted square pyramid. Two independent molecules are present in the asymmetric unit to form the π-stacked dimer by face-to-face overlap. Fluorescence quenching of $[Zn(L^1)(G^1)_2]$ is observed by intramolecular electron transfer from the pyrenyl moieties to the Zn^{II}-bound 4-nitrobenzoates.

Introduction

The organization of host molecules by complexation with metal ions has attracted much attention.[1] Metalloreceptors, which possess metal binding sites and additional interaction sites of ligands, have been regarded as useful organized host molecules.[2] Such metalloreceptors can undergo the desired conformational change for binding of guest molecules. The utilization of the allosteric effect is also a convenient approach to organize component molecules.[3]

A change in the fluorescent properties is generally considered to be a signal that a guest binding process has occurred.[4] The pyrene unit is one of the most commonly used fluorophores due to its strong luminescence and chemical stability.[5] Another interesting feature of the pyrene unit is the π-π interaction between pyrene aromatic rings in the crystal packing, which can permit the formation of highly ordered molecular aggregates in the solid state by architecturally controlled self-assembly.[6]

The complexation of a tridentate ligand with a Zn^{II} ion is expected to provide two labile coordination sites. Another advantage in the use of Zn^{II} as a binding site is its photophysical innocuousness and its Lewis acidity towards binding anions.[7] Flexible podand ligands allow metal complexes to possess a varied geometry at the metal center due to their different modes of coordination.[8] On this basis, the introduction of pyrene units, which serve as a fluorophore and provide an additional site for π-π interaction, into the podand moieties of a tridentate ligand should provide an efficient Zn^{II} metalloreceptor possessing a two-guest binding ability through first- and second-sphere coordination. In this context, we describe herein the structural characterization and fluorescence properties of Zn^{II} complexes composed of a tridentate ligand bearing podand pyrenyl moieties.

Results and Discussion

The tridentate podand ligand, 2,6-pyridinedicarboxaldehydebis(1-pyrenemethylimine) (L^1), which was obtained by Schiff base condensation of 2,6-pyridinedicarboxaldehyde with 1-pyrenemethylamine in methanol, was used to serve as a tridentate ligand bearing podand pyrenyl moieties as the fluorophore and additional interaction sites. Treatment of the tridentate podand ligand L^1 with $Zn(BF_4)_2$ led to the formation of the 2:1 complex $[Zn(L^1)_2(BF_4)_2]$ (Scheme 1), although the 1:1 complex $[Zn(L^1)(OAc)_2]$ was produced with $Zn(OAc)_2$.

The structure of the 2:1 complex $[Zn(L^1)_2(BF_4)_2]$ was confirmed by X-ray crystallography (Table 1). The crystal structure of $[Zn(L^1)_2(BF_4)_2]$ revealed that two tridentate podand ligands L^1 coordinate meridionally to Zn^{II} ion to give an orthogonally oriented molecular turn around an approximately octahedral Zn^{II} center (Figure 1). Selected bond lengths and bond angles are listed in Table 2. Six of their

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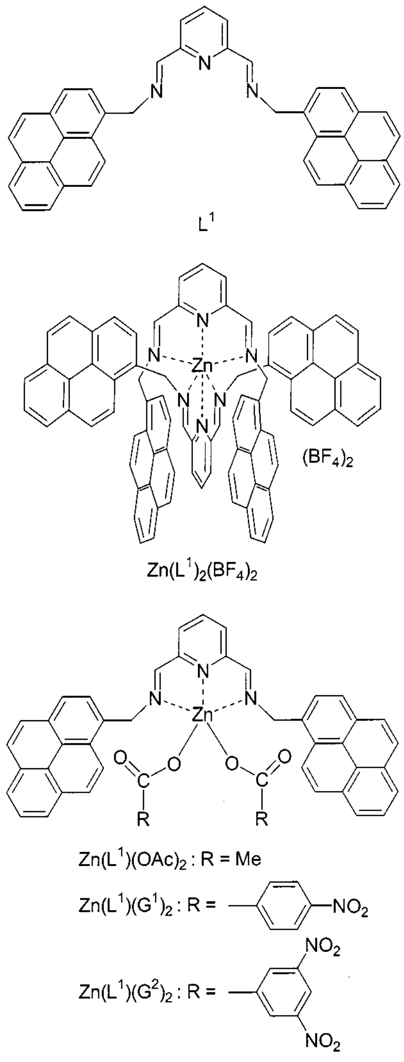

Scheme 1

Table 1. Crystallographic data for $[Zn(L^1)_2(BF_4)_2]$ and $[Zn(L^1)(G^1)_2]$

Empirical formula	$C_{82}H_{54}B_2F_8N_6Zn{\cdot}2CH_3OH$	$C_{55}H_{35}N_5O_8Zn$
Formula mass	1426.44	959.25
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$ (No. 14)	$P1$ (No. 1)
a [Å]	21.557(2)	12.4178(8)
b [Å]	17.783(2)	12.8828(8)
c [Å]	21.348(1)	15.7080(10)
α [°]		103.931(2)
β [°]	120.244(1)	110.1920(10)
γ [°]		100.0100(10)
V [Å^3]	7070.1(10)	2196.2(2)
Z	4	2
D_{calcd} [g cm^{-3}]	1.340	1.451
μ (Mo-K_α) [cm^{-1}]	4.23	6.26
T [°C]	23	25
λ(Mo-K_α) [Å]	0.71069	0.71073
$R1$[a] [$I > 2\sigma(I)$]	0.119	0.053
$wR2$[b] (all data)	0.371	0.084

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

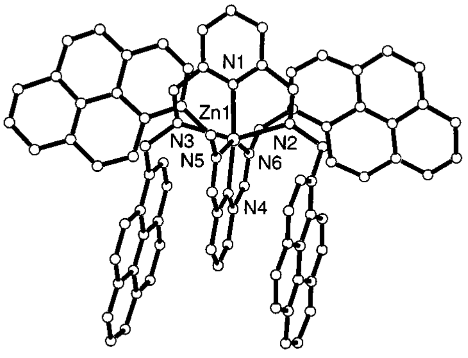

Figure 1. Molecular structure of $[Zn(L^1)_2(BF_4)_2]$ (hydrogen atoms and tetrafluoroborate ligands are omitted for clarity)

coordination sites are occupied by nitrogen donors of two pyridinedicarboxaldehydebisimine chelates. The N−Zn−N angles deviate from 90°, probably due to the formation of the five-membered chelate rings with extended conjugation. The most noteworthy structural feature is that one pyridyl moiety of L^1 is sandwiched between two podand pyrenyl moieties of another L^1 in a π-π interaction within which the distance between the pyridyl and pyrenyl moieties is ca. 3.5 Å. Furthermore, $[Zn(L^1)_2(BF_4)_2]$ shows extended π-stacking along a single axis in the crystal; the pyrenyl moieties are closely associated with the pyrenyl moieties of the neighboring molecules with ca. 3.5 Å separation and the remaining pyrenyl moieties surround the extended π-stacking through edge-to-face interaction with ca. 3.8 Å separation.

The coordinatively labile Zn^{II} center in $[Zn(L^1)(OAc)_2]$ bearing the tridentate podand ligand L^1 is able to provide two binding sites for two anions as guest molecules. The ancillary acetates were displaced by treatment of $[Zn(L^1)(OAc)_2]$ with the 4-nitrobenzoate ion (G^1), giving the 1:2 complex $[Zn(L^1)(G^1)_2]$ quantitatively. The 1:2 complex $[Zn(L^1)(G^2)_2]$ was obtained in a similar manner with the 3,5-dinitrobenzoate ion (G^2). The crystal structure of $[Zn(L^1)(G^1)_2]$ confirmed that $Zn(L^1)^{2+}$ accommodates two 4-nitrobenzoate ions and that two independent molecules are present in the asymmetric unit with almost the same conformation, as depicted in Figure 2. The structural parameter $\tau = (\beta - \alpha)/60$ for the coordination geometry of the five-coordinated complex proposed by Addison and Reedijik shows $\tau = 0.39$ and 0.33 for $[Zn(L^1)(G^1)_2]$, where α and β represent two basal angles ($\beta > \alpha$).[9] The parameters for an ideal square pyramidal and trigonal bipyramidal geometries are $\tau = 0$ ($\alpha = \beta = 180°$) and $\tau = 1$ ($\alpha = 120°$ and $\beta = 180°$), respectively. The τ values of $[Zn(L^1)(G^1)_2]$ indicate that the coordination geometry around Zn^{II} is a distorted square pyramid. Two imine nitrogens and two oxygens of the 4-nitrobenzoate moieties reside in the basal plane while one pyridyl nitrogen occupies the axial position. It is notable that two independent molecules overlap in a face-to-face manner to form a π-stacked dimer in which two 4-nitrobenzoate moieties lie in almost parallel planes and one pyrenyl moiety is sandwiched in-between. Furthermore, these π-stacked dimers are connected through

Table 2. Selected bond lengths [Å] and angles [°] for $[Zn(L^1)_2(BF_4)_2]$ and $[Zn(L^1)(G^1)_2]$

	$[Zn(L^1)_2(BF_4)_2]$	$Zn(L^1)(G^1)_2$ [a]	
Bond lengths			
Zn−N(1)	2.02(1)	2.043(11)	2.018(15)
Zn−N(2)	2.26(1)	2.254(14)	2.231(16)
Zn−N(3)	2.27(2)	2.211(15)	2.305(13)
Zn−N(4)	2.01(1)	−	−
Zn−N(5)	2.27(1)	−	−
Zn−N(6)	2.34(1)	−	−
Zn−O(1)	−	1.949(11)	1.976(10)
Zn−O(5)	−	1.871(10)	1.960(10)
Bond angles			
N(1)−Zn−N(2)	75.9(5)	73.5(5)	77.4(6)
N(1)−Zn−N(3)	73.3(6)	77.3(5)	71.9(5)
N(1)−Zn−N(4)	171.8(6)	−	−
N(1)−Zn−N(5)	107.2(4)	−	−
N(1)−Zn−N(6)	102.8(4)	−	−
N(2)−Zn−N(3)	149.2(5)	150.4(5)	149.1(5)
N(2)−Zn−N(4)	111.5(6)	−	−
N(2)−Zn−N(5)	94.9(4)	−	−
N(2)−Zn−N(6)	94.6(5)	−	−
N(3)−Zn−N(4)	99.3(7)	−	−
N(3)−Zn−N(5)	92.2(5)	−	−
N(3)−Zn−N(6)	94.1(4)	−	−
N(4)−Zn−N(5)	76.2(5)	−	−
N(4)−Zn−N(6)	73.8(5)	−	−
N(5)−Zn−N(6)	149.9(5)	−	−
N(1)−Zn−O(1)	−	127.2(4)	129.3(5)
N(1)−Zn−O(5)	−	121.6(5)	119.6(5)
N(2)−Zn−O(1)	−	95.0(5)	99.8(5)
N(2)−Zn−O(5)	−	102.0(5)	100.7(5)
N(3)−Zn−O(1)	−	99.0(5)	96.8(5)
N(3)−Zn−O(5)	−	97.0(5)	97.6(5)

[a] Two independent molecules exist in the asymmetric unit.

a π-π interaction with ca. 3.4 Å separation between the remaining pyrenyl moieties in the crystal.

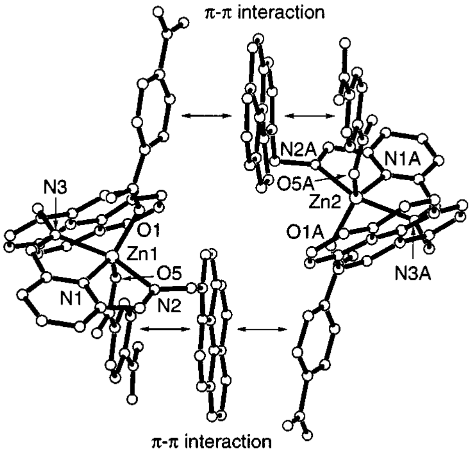

Figure 2. Molecular structure of $[Zn(L^1)(G^1)_2]$ (hydrogen atoms are omitted for clarity)

In the fluorescence spectra, the tridentate podand ligand L^1 shows both monomer and excimer emissions, as shown in Figure 3. $[Zn(L^1)(OAc)_2]$, on the other hand, only exhibits the monomer emission, due to a conformational change induced by complexation. Interestingly, fluorescence quenching was observed with $[Zn(L^1)(G^1)_2]$ by intramolecular electron transfer from the pyrenyl moieties to the Zn^{II}-bound 4-nitrobenzoates (Figure 4).[10] For the intramolecular electron-transfer process, the pyrenyl moieties and 4-nitrobenzoates should be close enough to each other for overlap of the orbitals. Both podand pyrenyl moieties are considered to interact with each Zn^{II}-bound 4-nitrobenzoate through π-π interactions by virtue of the flexibility of the podand pyrenylmethyl moieties in this system. The binding of two 3,5-dinitrobenzoates also resulted in fluorescence quenching in $[Zn(L^1)(G^2)_2]$.

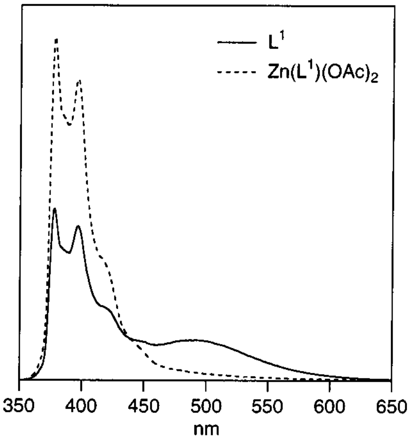

Figure 3. Fluorescence spectra of L^1 and $[Zn(L^1)(OAc)_2]$ in dichloromethane (1.0×10^{-5} M, $\lambda_{ex} = 344$ nm)

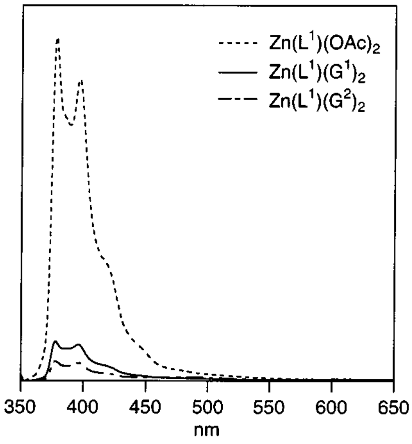

Figure 4. Fluorescence spectra of $[Zn(L^1)(OAc)_2]$, $[Zn(L^1)(G^1)_2]$, and $[Zn(L^1)(G^2)_2]$ in dichloromethane (1.0×10^{-5} M, $\lambda_{ex} =$ 344 nm)

Conclusion

The synthesis, structural characterization, and fluorescence properties of Zn^{II} complexes composed of a tridentate ligand bearing podand pyrenyl moieties have been described. The tridentate podand ligand L^1 forms the 2:1 complex $[Zn(L^1)_2(BF_4)_2]$ with $Zn(BF_4)_2$ and the 1:1 complex $[Zn(L^1)(OAc)_2]$ with $Zn(OAc)_2$. The aggregation of pyrenyl moieties through π-π interaction resulted in extended π-stacking, which permits architecturally controlled self-assembly in the solid state.

The coordinatively labile Zn^{II} center in $[Zn(L^1)(OAc)_2]$ provided a metalloreceptor possessing a two-guest binding ability. Fluorescence quenching by intramolecular electron transfer from the pyrenyl moieties to the guest molecules within $[Zn(L^1)(G)_2]$ was attained due to the flexibility of the podand moieties. Investigations on the scope of the allosteric metalloreceptor are currently in progress.

Experimental Section

General Methods: All reagents and solvents were purchased from commercial sources and were further purified by standard methods if necessary. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and are uncorrected. Infrared spectra were obtained with a Perkin−Elmer Model 1605 FT-IR. ^1H NMR spectra were recorded on a Varian Mercury 300 (300 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were run on a JEOL JMS-DX303HF mass spectrometer. Electronic spectra were obtained using a Shimazu MultiSpec-1500 photodiode array spectrophotometer. Fluorescence emission spectra were recorded using a Shimazu RF-5300PC spectrofluorophotometer and were not corrected for instrument response. Fluorescence emission measurements were carried out in degassed solvents at 25 °C.

Synthesis of 2,6-Pyridinedicarboxaldehydebis(1-pyrenemethylimine) (L^1): A mixture of 2,6-pyridinedicarboxaldehyde (0.27 g, 2.0 mmol), 1-pyrenemethylamine hydrochloride (1.07 g, 4.0 mmol), and triethylamine (1.4 mL, 10 mmol) in methanol (80 mL) was stirred under argon at room temperature for 3 h. The precipitate was collected by vacuum filtration and rinsed with methanol. The tridentate podand ligand L^1 was isolated in 96% yield by recrystallization from dichloromethane/ether. M.p. 196−198 °C (uncorrected). IR (KBr): $\tilde{\nu}$ = 1635, 1585 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.61 (d, J = 1.5 Hz, 4 H), 7.75 (t, J = 7.8 Hz, 1 H), 8.20−7.99 (m, 18 H), 8.37 (d, J = 9.0 Hz, 2 H), 8.51 (t, J = 1.5 Hz, 2 H). $C_{41}H_{27}N_3{\cdot}0.5H_2O$ (570.7): calcd. C 86.29, H 4.95, N 7.36; found C 86.65, H 4.86, N 7.31.

Preparation of $[Zn(L^1)_2(BF_4)_2]$: A mixture of L^1 (112 mg, 0.20 mmol) and $Zn(BF_4)_2$ (24 mg, 0.10 mmol) in acetonitrile (10 mL) was stirred under argon at room temperature for 3 h. After evaporation of the solution, $Zn(L^1)_2(BF_4)_2$ was isolated in 84% yield by recrystallization from acetonitrile/methanol. M.p. 246−247 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 1644, 1587 cm^{-1}. ^1H NMR (300 MHz, CD_3CN): δ = 4.88 (d, J = 1.5 Hz, 8 H), 6.09−5.99 (m, 6 H), 7.37 (d, J = 8.1 Hz, 4 H), 7.70 (t, J = 1.5 Hz, 4 H), 8.29−7.75 (m, 32 H). $C_{82}H_{54}B_2F_8N_6Zn{\cdot}2CH_3OH$ (1426.5): calcd. C 70.73, H 4.38, N 5.89; found C 70.53, H 4.11, N 6.12.

Preparation of $[Zn(L^1)(OAc)_2]$: A mixture of L^1 (169 mg, 0.30 mmol) and $Zn(OAc)_2$ (55 mg, 0.30 mmol) in dichloromethane (20 mL) was stirred under argon at room temperature for 3 h. Most of the dichloromethane solvent was evaporated, and $[Zn(L^1)(OAc)_2]$ was precipitated with ether. The precipitate was collected by vacuum filtration and dried to give $[Zn(L^1)(OAc)_2]$ in 98% yield. M.p. 173−174 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 1614, 1592 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.17 (s, 6 H), 5.96 (d, J = 1.5 Hz, 4 H), 7.31 (d, J = 7.8 Hz, 2 H), 7.77 (t, J = 1.5 Hz, 2 H), 7.85 (t, J = 7.8 Hz, 1 H), 8.26−8.01 (m, 18 H). $C_{45}H_{33}N_3O_4Zn{\cdot}H_2O$ (763.2): calcd. C 70.82, H 4.62, N 5.51; found C 70.79, H 4.69, N 5.47.

Preparation of $[Zn(L^1)(G^1)_2]$: A mixture of $[Zn(L^1)(OAc)_2]$ (75 mg, 0.10 mmol) and potassium 4-nitrobenzoate (40 mg, 0.20 mmol) in methanol (15 mL) was stirred under argon at room temperature for 3 h, resulting in a yellow precipitate. The precipitate was collected by vacuum filtration and dried to give a quantitative yield of $[Zn(L^1)(G^1)_2]$. M.p. 237−238 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 1632, 1590 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.73 (d, J = 1.5 Hz, 4 H), 8.16−7.66 (m, 29 H), 8.30 (br. t, 2 H). $C_{55}H_{35}N_5O_8Zn$ (959.3): calcd. C 68.86, H 3.68, N 7.30; found C 68.51, H 3.89, N 7.24.

Preparation of $[Zn(L^1)(G^2)_2]$: A mixture of $[Zn(L^1)(OAc)_2]$ (75 mg, 0.10 mmol) and potassium 3,5-dinitrobenzoate (47 mg, 0.20 mmol) in methanol (15 mL) was stirred under argon at room temperature for 3 h, resulting in a yellow precipitate. The precipitate was collected by vacuum filtration and dried to give a quantitative yield of $[Zn(L^1)(G^2)_2]$. M.p. 256−257 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 1626, 1591 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.55 (d, J = 1.5 Hz, 4 H), 8.17−7.76 (m, 24 H), 8.36 (t, J = 2.1 Hz, 2 H), 8.38 (t, J = 7.8 Hz, 1 H), 8.75 (br. t, 2 H). $C_{55}H_{33}N_7O_{12}Zn{\cdot}2H_2O$ (1085.33): calcd. C 60.87, H 3.44, N 9.03; found C 60.47, H 3.38, N 8.74.

X-ray Crystal Structure Determination: The measurement for $[Zn(L^1)_2(BF_4)_2]$ was made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite-monochromated Mo-K_α radiation. A total of 56986 independent reflections was obtained of which 15981 were unique. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. $R1$ = 0.119, $wR2$ = 0.371. The measurement for $[Zn(L^1)(G^1)_2]$ was made on a Bruker SMART 1000 diffractometer with graphite-monochromated Mo-K_α radiation. A total of 12923 independent reflections were obtained of which 10897 were unique. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. $R1$ = 0.053, $wR2$ = 0.084. Crystallographic details are given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-169877 for $[Zn(L^1)_2(BF_4)_2]$ and CCDC-169878 for $[Zn(L^1)(G^1)_2]$. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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[10] An electron transfer process from the pyrenyl moiety to the 4-nitrobenzoate moiety is thermodynamically feasible, as indicated by the negative value of $\Delta G_{\mathrm{ET}} = E(\mathrm{D}^+/\mathrm{D}) - E(\mathrm{A}/\mathrm{A}^-) - E^{0-0} = -0.6$ eV.

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