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Synthesis and Characterization of 3,5-Bis(2-hydroxyphenyl)-1,2,4-triazole Functionalized Tetraaryloxy Perylene Bisimide and Metal-Directed Self-Assembly

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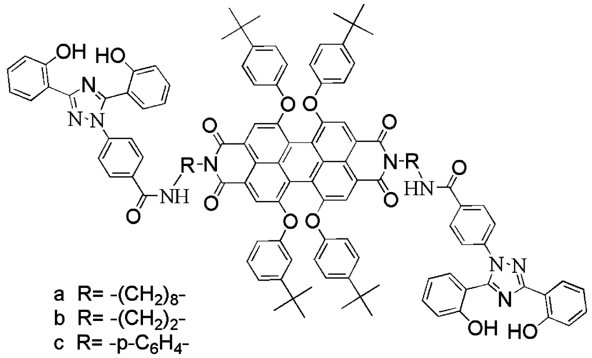

New perylene bisimide dyes bearing 3,5-bis(2-hydroxyphenyl)-1,2,4-triazole receptor units with different spacers have been synthesized and characterized. The fluorescence and electronic properties of these compounds have been studied. MALDI-TOF, UV−vis, and fluorescence titration experiments proved that monotopic perylene bisimide ligands could be assembled into dimmers by Fe^{III} coordination. The coordination properties of the ditopic perylene bisimide ligands have also been studied preliminarily. Furthermore, the SEM images indicated that well-defined nanoscale structures could be fabricated by self-assembly due to metal ion coordination and π−π stacking interactions of perylene rings with the help of a proper spacer.

Introduction

Supramolecular polymers, chains of molecules connected by noncovalent bonds, have attracted considerable interest in recent years.[1−6] They have many properties in common with ordinary, covalent polymers but also introduce new features. Metal-mediated self-assembly has been proved to be a very effective methodology in constructing two- or three-dimensional supramolecular architectures, such as macrocycles, molecular containers, tubular structures, interlocked and intertwined structures, and helicates, which are useful in molecular or chiral recognition, host−guest chemistry, catalysis, and memory storage.[7,8]

A number of coordination polymers have been synthesized mostly based on kinetically inert complexes.[9] Introduction of metal ions into conjugated polymers has

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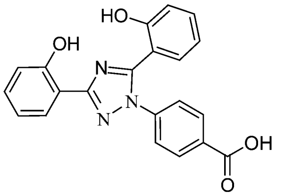
been investigated with regard to higher electroluminescence quantum yields by harvesting triplet state emission.[10] Thus metal-directed supramolecular polymerization of photoactive building blocks might be of interest.[11] Red chromophores based on perylenetetracarboxylic diimide recently triggered considerable attention of investigators and show possible various applications such as fluorescent solar collectors,[12] photovoltaic devices,[13] dye lasers,[14] molecular switches,[15] and light emitting diodes[16] due to their exclusive chemical, thermal, and photochemical stability and their ability to self-assemble into extended structures.[17] They are highly absorbing in the visible to near-IR region ($\epsilon \approx 10^5$ M^{-1} cm^{-1}) and emit fluorescene with quantum yields near unity.[18] Perylene-based chromophoric arrays[19] are promising components for the construction of optical and electronic molecular devices, for instance as n-type semiconductor material in organic photovoltaic cells.[20] They have been incorporated in classical polyimide main chain polymers by the Müllen and Thelakkat groups.[18a,21] The Würthner group has studied metal-directed self-assembly of highly fluorescent perylene bisimides equipped with the 2,2′:6′,2″-terpyridine complexing unit[11,22] to photoactive coordination polymers.

The tridentate ligand 4-[3,5-bis(2-hydroxyphenyl)-1,2,4-triazol-1-yl] benzoic acid (H_3L),[23] as a potential ligand for the construction of larger polymeric aggregates, has been shown in the literature to bind metal ions using the two deprotonated phenolic hydroxyl groups and one of the nitrogen atoms of the heterocycle.[24] Formation of the 2:1 HL (-2H)-Fe^{3+} complex has a log K value of 38.6 in H_2O/DMSO (4:1), and this complex adopts a *trans*-N_2O_4 coordination.[24] H_3L has also a strong affinity for Al^{3+} (log $K = 34.0$), Cu^{2+} (log $K = 23.9$), and Zn^{2+} (log $K = 17.5$) ions.



H_3L

Here we report the metal-directed self-assembly of perylenetetracarboxylic diimide connected to ligand H_3L through different spacers, which provided the opportunity to elucidate the impact of the metal ion and spacers on the photophysical properties of perylenetetracarboxylic diimide and on the nanostructure of these self-assembling photofunctional materials. For reasons of comparison and simplicity, we also prepared monotopic perylene.

Results and Discussion

Synthesis and Characterization of Perylene Bisimide Ligands. A mixture of **2** and **5** was obtained by partial saponification of the corresponding *N,N′*-dioctyl perylene bisimide (**1**).[25] Monoanhydride **2** or bisanhydride **5** was condensed with corresponding diamine in toluene with the catalysis of imidazole[26] to afford **3** or **6**. The dyes **6** with two amino anchor groups were linked to the appropriate carboxylic acid chloride of ligand H_3L so that the ditopic perylene bisimides **7** were obtained (Scheme 1). The same reaction starting with the dyes **3** afforded the monotopic perylene bisimide ligands **4**. For **4a**, **4b**, **7a**, and **7b**, the spacer units R had flexable -CH$_2$- linkages, while for **4c** and **7c**, the rigid backbone was derived from phenylene group. The new compounds were fully characterized by ^{1}H NMR and ^{13}C NMR and MALDI-TOF mass spectroscopy.

Ligands **4** and **7** are dark purplish-black solids that, once dissolved homogeneously, display the typical bright red color that is representative for tetraphenoxy-substituted perylene bisimides. The optical absorption and fluorescence properties of the ligands **4** and **7** and their relative fluorescence quantum yields ϕ_F were investigated.

The UV–vis absorption spectra of **4** and **7** showed almost unchanged absorption properties of the perylene bisimide upon linkage with the ligand at wavelengths $\lambda > 350$ nm (representative spectra are shown in Figure 1, and the absorption data are summarized in Table 1). The absorption bands of the perylene unit gave the characteristic $\pi-\pi$ transitions of the functionalized perylene bisimide:[27,28] 455 nm (S_0-S_2 electronic transi-

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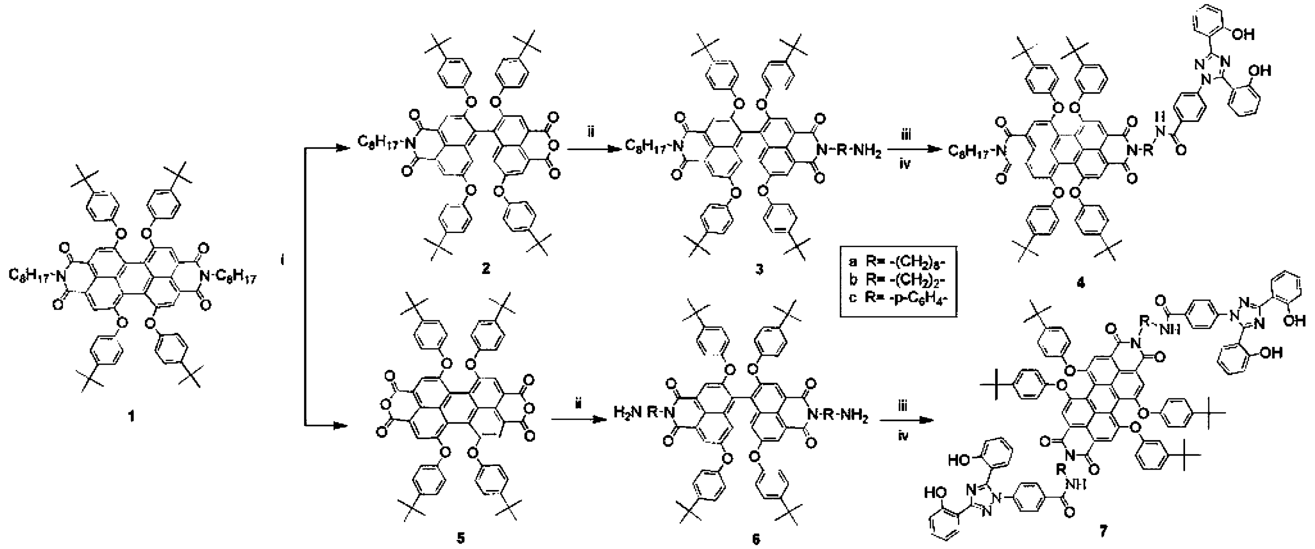
SCHEME 1. Synthesis Route of the Functioned Perylene Bisimide Dyes[a]



[a] (i) KOH, isopropyl alcohol, H_2O, reflux, 10 h; (ii) diamine, toluene, imidazole, reflux, 0.5 h; (iii) H_3L, $SOCl_2$, THF; (iv) Et_3N, THF, $CHCl_3$.

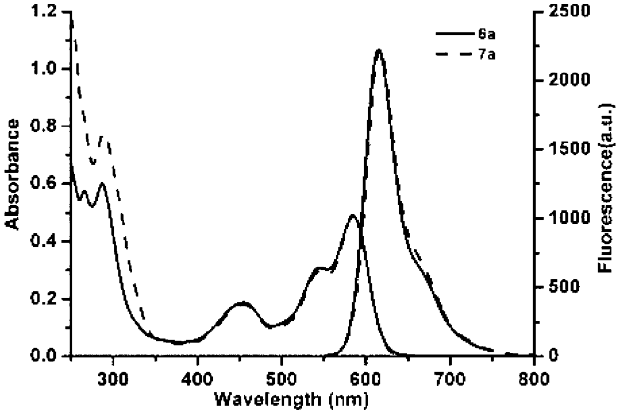


FIGURE 1. UV–vis absorption and fluorescence spectra of diamino-perylene **6a** and ditopic perylene bisimide ligand **7a** (10^{-5} M) in $CHCl_3$.

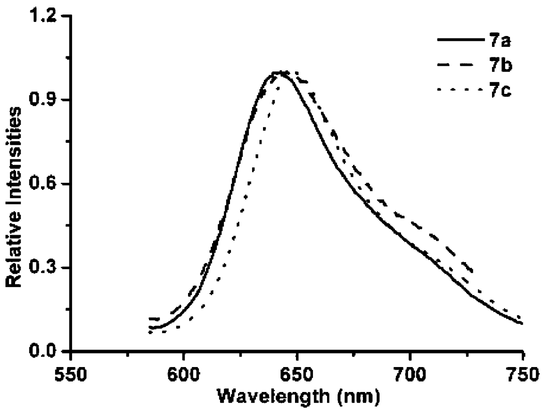


FIGURE 2. Normalized fluorescence spectra of **7a**, **7b**, and **7c** in solid film (λ_{exc} = 550 nm).

TABLE 1. Photophysics of Perylene Bisimide Ligand

	UV λ_{max} (nm) (ϵ dm^3 mol^{-1} cm^{-1})	FL λ_{max} (nm)	ϕ_F[a]
4a	585 (46650)	623	0.91
4b	593 (44320)	617	0.81
4c	589 (41160)	614	0.88
7a	585 (46650)	614	0.88
7b	589 (47900)	620	0.75
7c	587 (51060)	615	0.90

[a] *N,N'*-Di(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4,9,10-tetracarboxylic diimide (TPPI) as reference (ϕ_{fl} = 0.96 in $CHCl_3$).[14b]

tion), 545 and 585 nm (S_0–S_1 electronic transition).[14b,29] At shorter wavelengths, a small increase in the absorption attributed to triazol ligand can be observed. The fluorescence peaks obtained for the fluorescent perylene bisimide **4** and **7** in chloroform are mirror images of the S_0–S_1 absorption band, and their position and vibronic fine structure corresponded well to those unlinked with triazol-ligand. The fluorescence quantum yields (ϕ_F) ranged from 0.75 for **7b** to 0.91 for **4a** in $CHCl_3$. Particularly, the fluorescence spectra of **7a**, **7b**, and **7c** as thin film show red emission at 642, 646, and 649 nm, respectively (Figure 2). The spacer between the H_3L ligands and the perylene bisimide affected the fluorescence of the core perylene bisimide. These sorts of compounds can be used as good red emission materials.

Synthesis and Characterization of Perylene Bisimide Ligand–Metal Complexes. The complexation of the monotopic dye **4** with Fe^{III} yields a dimeric complex, which could be seen as a model reaction for the formation of the coordination polymer. Complexation with Fe^{III} could be achieved in a mixture of chloroform and methanol and can be easily demonstrated by means of MALDI-TOF mass spectrometry, UV–vis spectroscopy, and fluorescence titration experiments. Addition of Fe^{3+} to the solution of **4a** led to a modification of the absorption

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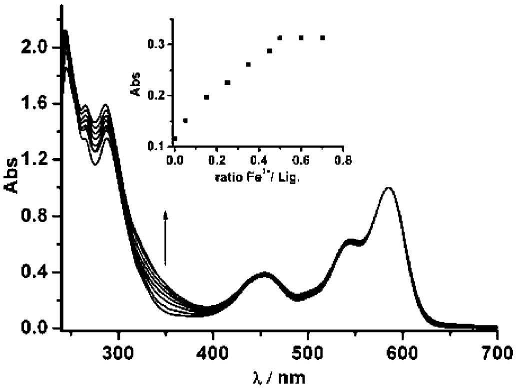

FIGURE 3. UV–vis absorption titration experiment of **4a** (10^{-5} M) in $CHCl_3$ with Fe $(NO_3)_3$; inset shows absorbance change (at 350 nm) as a function of the Fe^{3+}/ligand ratio.

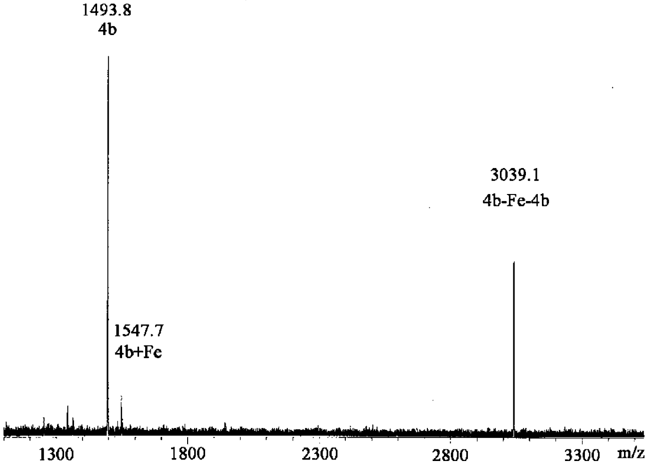

FIGURE 4. MALDI-TOF spectrogram of the **4b**-Fe-**4b** coordination dimmer.

spectra with an increase of the absorbance at 350 nm, almost unchanged absorption properties at wavelengths $\lambda > 400$ nm (as shown in Figure 3), and a change of the color of the solution from red to violet. The MALDI-TOF mass spectrogram of **4b**-Fe^{III} complex showed a clear dimeric complex (Figure 4), which indicated that with Fe^{III} this ligand preferred to form bis complex $[FeL_2]^{3-}$, whereas in the case of ditopic perylene bisimide **7**, only fragments showing the ligand with one Fe^{3+} could be observed. (The mass fractions of higher-molecular-weight oligomers or polymers were absent due to the opening of the iron(III)–H_3L complexes under the MALDI conditions or insufficient desorption.)[30] The initial solubility of coordination polymers was good in chloroform/methanol, but they slowly started to precipitate within 1 day after preparation, which suggested that the polymers were consolidating, thereby increasing their molecular weight.[22b]

The fluorescence titration experiment showed the fluorescence quenching of perylene bisimide in the presence of Fe^{III} (Figure 5). In particular, upon addition of Fe^{III} to the solution of **4** in 1:2 ratio, the fluorescence of perylene almost quenched completely, which indicated the formation of dimeric complex. Similar results were obtained for **7b**-Fe^{III} complex. According to these UV–vis and fluorescence spectra, there were evident electronic interactions between the FeL_2 unit and the perylene bisimide chromophore: Fe^{III} as a good electron acceptor quenched the excited state of the perylene bisimide through electron transfer.

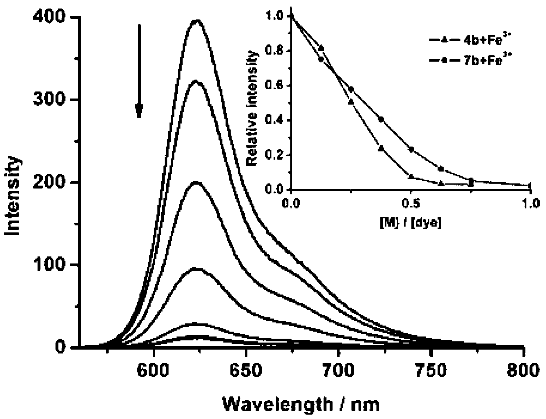

FIGURE 5. Fluorescence titration experiment of **4b** (10^{-5} M) in $CHCl_3/CH_3OH$ (100:1) with Fe $(NO_3)_3$, λ_{exc}=550 nm. Inset: relative fluorescence intensities upon addition of $Fe(NO_3)_3$ calculated from the integrated fluorescence spectra.

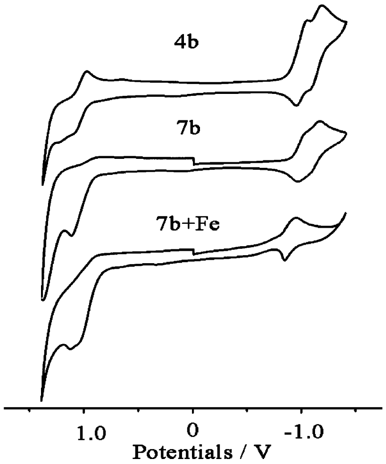

FIGURE 6. Cyclic voltammograms of **4b**, **7b**, and **7b** + Fe^{3+} in 0.05 M $TBAPF_6$, $CHCl_3$. Scan rate = 50 mV/s.

Electrochemical Properties of Perylene Bisimide Ligand–Metal Complexes. The electrochemical properties of the polymers and model compounds were also studied. The representative cyclic voltammograms were shown in Figure 6. In the cathodic scans, **4b**, **7b** exhibited quasireversible reduction waves at $E_{1/2}$ values of −0.98 and −1.12 V; **7b**-Fe showed a wave at −0.89 V. These waves were attributed to the reduction of perylene bisimide moieties. In the anodic scans, oxidation peak of **4b** at 1.05 V was observed. **7b** showed an irreversible wave at 1.12 V, wehreas when complexed with Fe, a more negative oxidation peak at 1.05 V appeared. These data showed that the electrochemical properties of the Fe-complexed perylene bisimide ligands were improved compared with that of noncomplexed ligands: their energy gaps between the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LOMO) decreased (Table 2). It is clear that the spacer unit R (rigid phenylene group, flexible -CH_2-

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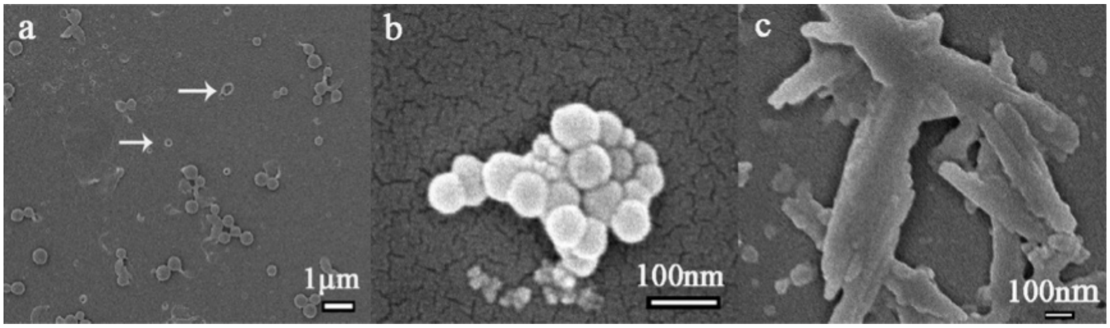

FIGURE 7. Scanning electron micrograph (SEM) images of self-assembled **7a**-Fe (a), **7b**-Fe (b), and **7c**-Fe (c) coordination polymers in $CHCl_3$.

TABLE 2. Electrochemical Properties of Perylene Bisimide Ligand and Fe(III) Complexes

	oxidation	reduction		
	$E_{1/2}$	$E_{1/2}$ (1)	$E_{1/2}$ (2)	band gap (eV)[a]
4a	1.08	−0.98	−1.11	1.85
4b	1.05	−0.98	−1.12	1.84
4c	1.36	−0.80	−0.95	1.95
7a	1.13	−0.99	−1.09	1.83
7b	1.12	−0.98	−1.12	1.83
7c	1.31	−0.81	−0.94	1.93
4b + Fe	1.02	−0.91		1.64
7a + Fe	1.03	−0.85		1.62
7b + Fe	1.05	−0.89		1.65
7c + Fe	1.14	−0.72		1.57

[a] Gained from the E_{onset}.

linkages) have evident influence on the electrical properties of these compounds in the ground state. Both compounds with flexible -CH_2- linkages exhibit nodes at the imide N atoms,[31] which indicate that the substituents at those positions do not influence the energy levels of the compounds, so the electronic properties of those with flexible -CH_2- linkages, no matter long or short, are similar. In contrast, those with rigid phenylene linkages became easier to reduce but more difficult to oxidize.

SEM Images of Perylene Bisimide Ligand−Metal Complexes. It was clear that the spacer unit R (rigid phenylene group, flexible -CH_2- linkages) had evident influence on the optical and electrical properties in the ground state and great influence on the nanostructure of these self-assembling photofunctional materials. Figure 7 showed the scanning electron micrograph (SEM) images of self-assembled **7a**-Fe, **7b**-Fe, and **7c**-Fe coordination structures in $CHCl_3$. From the electron micrograph images in Figure 7 it was sure that **7a**-Fe tended to form capsule-like structures with diameters in the range of 200−300 nm (arrows indicate the broken ones), **7b**-Fe formed one-dimensional ball-like supramolecular structures with diameters around 50 nm, and **7c**-Fe self-assembled aggregates tend to form rod-like supramolecular structures with diameters in the range of 50−100 nm, whose lengths were extended to 1−2 μm and which tended to aggregate into bigger rods. These aggregates mainly resulted from the $\pi-\pi$ stacking interactions of perylene rings, and the spacers between the ligands and perylene bisimide affected the aggregates structures.

Conclusion

In conclusion, new perylene bisimide dyes connected with 3,5-bis(2-hydroxyphenyl)-1,2,4-triazole (H_3L) receptor units through different spacers have been synthesized and characterized successfully. The spacer between the H_3L ligands and the perylene bisimide affected the fluorescence of the core perylene bisimide, and this sort of compound can be used as good red emission materials. MALDI-TOF mass spectrometry, UV−vis spectroscopy, and fluorescence titration experiments proved that monotopic perylene bisimide ligands could be assembled to nonfluorescent dimmers by Fe^{III} ion coordination. The coordination properties of the ditopic perylene bisimide ligands have also been investigated preliminarily, and the study of the polymer structure is underway. The electrochemical studies showed that the electronic properties of those with flexible -CH_2- linkages are similar; in contrast, those with rigid phenylene linkages became easier to reduce but more difficult to oxidize. The band gaps of the Fe-complexed perylene bisimide ligands decreased compared with those of noncomplexed ligands. Furthermore, the SEM images indicated that well-defined nanoscale structures could be fabricated by self-assembly due to metal ion coordination and $\pi-\pi$ stacking interactions of perylene rings with the help of a proper spacer.

Experimental Section

***N,N′*-Dioctyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic Diimide (1).** Prepared from 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic acid bisanhydride according to literature[25b] but with octylamine. ^1H NMR (400 M, $CDCl_3$, TMS), δ 8.22(s, 4 H), 7.22(d, 8 H), 6.82(d, 8 H), 4.10(t, 4 H), 1.66(m, 4 H), 1.36(m, 4 H), 1.29(s, 44 H), 0.86(t, 6 H). IR spectrum (KBr) ν = 3057, 2959, 2927, 2861, 1697, 1660, 1589, 1504, 1410, 1349, 1289, 1218, 1173, 1112, 1018, 881, 838, 733, 554 cm^{-1}. MALDI-TOF calcd 1206.7, obsd 1221.7. Anal. Calcd for $C_{80}H_{90}N_2O_8$: C, 79.57; H, 7.51; N, 2.32. Found: C, 79.02; H, 7.57; N, 2.19.

***N*-Octyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4-anhydride-9,10-tetracarboxylic Imide (2) and 1,6,7,12-Tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic Bisanhydride (5).** *N,N′*-Dioctyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic diimide (3.6 g, 3.0 mmol) with KOH (6 g, 10 mmol) in isopropyl alcohol (60 mL) and H_2O (3 mL) under argon by stirring at reflux for 10 h, followed by acidic workup and thorough washing and drying, yielded a mixture (3.0 g) of perylene bisanhydride (**5**) and perylene mono octylimide (**2**) in a ratio of about 7:3. **2** and **5** were separated by column chromatography on a silica gel with CH_2Cl_2/petroleum ether (1:2).

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(31) Langhals, H.; Demmig, S.; Huber, H. *Spectrochim. Acta, Part A* **1988**, *44A*, 1189.

***N*-Octyl-*N*′-(8-aminooctyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic Diimide (3a).** Perylene monooctylimide **2** (0.28 g, 0.25 mmol), 1,8-diaminooctane (0.36 g, 2.5 mmol), and imidazole(100 mg) were stirred under argon at reflux for 0.5 h in toluene (80 mL). The reaction mixture was washed with water twice and then dried over anhydrous sodium sulfate. The solvent was removed in vacuo. Purification was carried out by column chromatography on a silica gel with $\mathrm{CHCl_3}$ as eluent, affording **3a** (0.21 g, 70% yield). ^{1}H NMR (400 M, $\mathrm{CDCl_3}$, TMS), δ 8.22 (s, 4 H), 7.23 (d, 8 H, J = 8.0 Hz), 6.82 (d, 8 H, J = 8.0 Hz), 4.09 (t, 4 H, J = 7.1 Hz), 2.67 (t, 2 H, J = 6.9 Hz), 2.0 (br, $-\mathrm{NH_2}$), 1.66 (m, 4 H), 1.42 (m, 2 H), 1.29 (m, 54 H), 0.85 (t, 3 H, J = 6.7 Hz). IR spectrum (KBr) ν = 3041, 2959, 2928, 2859, 1698, 1661, 1590, 1504, 1436, 1411, 1351, 1286, 1216, 1173, 1111, 1016, 879, 837, 554 cm^{-1}. UV−vis ($\mathrm{CHCl_3}$): λ_{max}/nm = 584, 543, 453. MALDI-TOF calcd 1222.6, obsd 1221.7. Anal. Calcd for $\mathrm{C_{80}H_{91}N_3O_8}$: C, 78.59; H, 7.50; N, 3.44. Found: C, 78.51; H, 7.48; N, 3.49.

***N*-Octyl-*N*′-(2-aminoethyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic Diimide (3b).** Perylene monooctylimide **2** (0.28 g, 0.25 mmol), 1,2-ethylenediamine (0.075 g, 2.5 mmol), and imidazole (100 mg) were allowed to react in the same way as described for **3a** and purified by column separation (silica gel, chloroform) to yield **3b** (213 mg, 75%). ^{1}H NMR (400 M, $\mathrm{CDCl_3}$, TMS), δ 8.22 (s, 2 H), 8.21 (s, 2 H), 7.22 (d, 8 H, J = 8.7 Hz), 6.82 (dd, 8 H, 2.3 Hz, 8.3 Hz), 4.5 (br, $-\mathrm{NH_2}$), 4.23 (t, 2 H, J = 6.2 Hz), 4.09 (t, 2 H, J = 7.0 Hz), 3.04 (t, 2 H, J = 6.0 Hz), 1.66 (m, 2 H), 1.28 (m, 46 H), 0.84 (t, 3 H, J = 6.2 Hz). IR spectrum (KBr) ν = 3375, 3062, 2960, 2868, 1699, 1662, 1589, 1504, 1434.8, 1411, 1347, 1286, 1216, 1174, 1112, 1016, 880, 837, 754, 555 cm^{-1}. UV−vis ($\mathrm{CHCl_3}$): λ_{max}/nm = 587, 547, 459. MALDI-TOF calcd 1138.4, obsd 1137.7. Anal. Calcd for $\mathrm{C_{74}H_{79}N_3O_8}$: C, 78.07; H, 6.99; N, 3.69. Found: C, 77.95; H, 6.92; N, 3.63.

***N*-Octyl-*N*′-(4-aminophenyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic Diimide (3c).** Perylene mono octylimide **2** (0.28 g, 0.25 mmol), benzene-1,4-diamine (0.27 g, 2.5 mmol), and imidazole (100 mg) were allowed to react in the same way as described for **3a** and purified by column separation (silica gel, $\mathrm{CH_2Cl_2}$) to yield **3c** (228 mg, 77%). ^{1}H NMR (400 M, $\mathrm{CDCl_3}$, TMS), δ8.23 (s, 2 H), 8.21 (s, 2 H), 7.22 (m, 8 H), 7.10 (d, 2 H, J = 8.3 Hz), 7.04 (m, 2 H), 6.83 (m, 8 H), 4.10 (t, 2 H, J = 7.0 Hz), 1.66 (m, 2 H), 1.33 (m, 2 H), 1.26 (s, 44 H), 0.85 (t, 3 H, J = 6.7 Hz). IR spectrum (KBr) ν = 3374, 3041, 2958, 2864, 1699, 1663, 1588, 1505, 1409, 1341, 1287, 1213, 173, 1109, 1014, 833, 731, 552 cm^{-1}. UV−vis ($\mathrm{CHCl_3}$): λ_{max}/nm = 584, 541, 453. MALDI-TOF calcd 1186.5, Observed, 1185.3. Anal. Calcd for $\mathrm{C_{78}H_{79}N_3O_8}$: C, 78.96; H, 6.71; N, 3.54. Found: C, 78.75; H, 6.67; N 3.48.

***N*,*N*′-Di(8-aminooctyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic Diimide (6a).** Perylene bisanhydride **5** (0.50 g, 0.5 mmol), 1,8-diaminooctane (0.72 g, 5 mmol), and imidazole (200 mg) were stirred under argon at reflux for 0.5 h in toluene (80 mL). The reaction mixture was washed with water twice and then dried over anhydrous sodium sulfate. The solvent was removed in vacuo. Purification was carried out by column chromatography on a silica gel with $\mathrm{CHCl_3}$/methanol (10:1) as eluent, affording **6a** (0.42 g, 68% yield). ^{1}H NMR (400 M, $\mathrm{CDCl_3}$, TMS), δ 8.21 (s, 4 H), 7.22 (d, 8 H, J = 8.1 Hz), 6.82 (d, 8 H, J = 8.0 Hz), 4.08 (m, 4 H), 2.66 (t, 4 H, J = 6.6 Hz), 1.80 (br, $-\mathrm{NH_2}$), 1.65 (m, 8 H), 1.29 (m, 52 H). UV−vis ($\mathrm{CHCl_3}$): λ_{max}/nm = 585, 542, 454. MALDI-TOF calcd 1237.6, obsd 1237.1. Anal. Calcd for $\mathrm{C_{80}H_{92}N_4O_8}$: C, 77.64; H, 7.49; N, 4.53. Found: C, 76.98; H, 7.44; N, 4.50.

***N*,*N*′-Di(2-aminoethyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic Diimide (6b).** Perylene bisanhydride **5** (0.50 g, 0.5 mmol), 1,2-ethylenediamine (0.15 g, 5 mmol), and imidazole (200 mg) were allowed to react in the same way as described for **6a** and purified by column separation (silica gel, chloroform/methanol 10:1) to yield **6b** (345 mg, 65%). ^{1}H NMR (400 M, $\mathrm{CDCl_3}$, TMS), δ 8.22 (s, 4 H), 7.03 (d, 8 H, J = 8.7 Hz), 6.82 (d, 8 H, J = 8.7 Hz), 4.21 (t, 4 H, J = 6.4 Hz), 3.01 (t, 4 H, J = 6.4 Hz), 1.29 (s, 36 H). IR spectrum (KBr) ν = 3389, 3041, 2960, 2867, 1699, 1662, 1589, 1504, 1434, 1410, 1347, 1285, 1215, 1174, 1109, 1016, 878, 836, 803, 554 cm^{-1}. UV−vis ($\mathrm{CHCl_3}$): λ_{max}/nm = 586, 543, 455. MALDI-TOF calcd 1069.2, obsd 1068.8. Anal. Calcd for $\mathrm{C_{68}H_{68}N_4O_8}$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.03; H, 6.37; N, 5.19.

***N*,*N*′-Di(4-aminophenyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic Diimide (6c).** Perylene bisanhydride **5** (0.50 g, 0.5 mmol), benzene-1,4-diamine (0.54 g, 5 mmol), and imidazole (200 mg) were allowed to react in the same way as described for **6a** and purified by column separation (silica gel, $\mathrm{CH_2Cl_2}$) to yield **6c** (435 mg, 75%). ^{1}H NMR (400 M, $\mathrm{CDCl_3}$, TMS), δ 8.23 (s, 4 H), 7.22 (d, 8 H, J = 8.7 Hz), 7.00 (d, 4 H, J = 8.5 Hz), 6.83 (d, 8 H, J = 8.6 Hz), 6.76 (d, 4 H, J = 8.5 Hz), 1.60 (br, $-\mathrm{NH_2}$), 1.26 (s, 36 H). IR spectrum (KBr) ν = 3377, 3042, 1702, 1667, 1587, 1507, 1407, 1341, 1286, 1208, 1174, 881, 834, 553 cm^{-1}. UV−vis ($\mathrm{CHCl_3}$): λ_{max}/nm = 584, 545, 453. MALDI-TOF calcd 1165.3, obsd 1164.2. Anal. Calcd for $\mathrm{C_{76}H_{68}N_4O_8}$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.17; H, 5.81; N, 4.74.

Ligand Derivative 4a. 4-[3,5-Bis(2-hydroxyphenyl)-1,2,4-triazol-1-yl] benzoyl chloride (0.2 mmol) and *N*-octyl-*N*′-(8-aminooctyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic diimide (**3a**) (122 mg, 0.10 mmol) were allowed to react according to the general procedure and purified by column separation (silica gel, $\mathrm{CH_2Cl_2}$) to yield a black powder (55 mg, 35%). ^{1}H NMR (400 M, $\mathrm{CDCl_3}$, TMS), δ 8.21 (s, 4 H), 8.12 (dd, 1 H, J = 7.8 Hz, 1.5 Hz), 7.93 (d, 2 H, J = 8.5 Hz), 7.57 (d, 2 H, J = 8.5 Hz), 7.37−7.30 (m, 2 H), 7.22 (d, 8 H, J = 8.7 Hz), 7.12 (d, 1 H, J = 8.4 Hz), 7.05 (m, 2 H), 6.91 (dd, 1 H, J = 8.0 Hz, 1.4 Hz), 6.82 (d, 8 H, J = 8.6 Hz), 6.64 (t, 1 H, J = 7.2 Hz, 8.1 Hz), 6.17 (t, 1 H, J = 5.0 Hz, 5.7 Hz), 4.10 (m, 4 H), 3.48 (m, 2 H), 1.66 (m, 6 H), 1.36 (m, 10 H), 1.28 (s, 36 H), 1.25 (m, 8 H), 0.84 (t, 3 H, J = 7.0 Hz). ^{13}C NMR (100 M, $\mathrm{CDCl_3}$, TMS), δ165.9, 163.3, 159.4, 157.9, 156.3, 155.8, 155.7, 152.7, 151.9, 147.1, 140.1, 136.3, 132.8, 132.7, 132.7, 131.6, 128.5, 127.5, 127.4, 126.5, 126.1, 122.4, 122.2, 120.4, 120.3, 119.7, 119.3, 119.2, 118.9, 118.3, 116.9, 113.0, 109.7, 40.5, 40.4, 40.2, 34.2, 31.6, 31.3, 29.4, 29.1, 29.0, 28.9, 27.9, 27.8, 27.0, 26.8, 26.7, 22.5, 13.9. IR spectrum (KBr) ν = 3306, 3062, 2958, 2860, 1698, 1660, 1589, 1504, 1463, 1411, 1351, 1285, 1215, 1171, 1111, 1016, 836, 754, 554 cm^{-1}. UV−vis ($\mathrm{CHCl_3}$): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 585 (46650), 545 (28030), 454 (17100), 287 (63460). Fluorescence ($\mathrm{CHCl_3}$): λ_{max}/nm = 623.1, fluorescence quantum yield (λ_{exe} = 550 nm, E_{550nm} = 0.0414/1 cm, $\mathrm{CHCl_3}$, reference *N*,*N*′-bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4,9,10-tetracarboxylic diimide (TPPI) with Φ = 0.96 in $\mathrm{CHCl_3}$) = 0.91. MALDI-TOF calcd 1577.9, obsd 1577.9. Anal. Calcd for $\mathrm{C_{101}H_{104}N_6O_{11}}$: C, 76.88; H, 6.64; N, 5.33. Found: C, 76.53; H, 6.58; N, 5.41.

Ligand Derivative 4b. 4-[3,5-Bis(2-hydroxyphenyl)-1,2,4-triazol-1-yl] benzoyl chloride (0.2 mmol) and *N*-octyl-*N*′-(2-aminoethyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic diimide (**3b**) (113 mg, 0.10 mmol) were allowed to react according to the general procedure and purified by column separation (silica gel, $\mathrm{CH_2Cl_2}$) to yield a black powder (60 mg, 40%). ^{1}H NMR (300 M, $\mathrm{CDCl_3}$, TMS), δ 9.50 (bs, 1 H), 8.27 (s, 2 H), 8.20 (s, 2 H), 8.14 (dd, 1 H, J = 8.1 Hz, 1.4 Hz), 7.90 (d, 2 H, J = 8.4 Hz), 7.51 (d, 2 H, J = 8.3 Hz), 7.39 (m, 1 H), 7.20 (m, 8 H), 7.15−7.02 (m, 3 H), 6.86 (dd, 1 H, J = 8.0 Hz, 1.2 Hz), 6.80 (dd, 8 H, J = 8.7 Hz, 2.0 Hz), 6.60 (m, 1 H), 4.52 (m, 2 H), 4.09 (m, 2 H), 3.90 (m, 2 H), 1.66 (m, 2 H), 1.32 (m, 2 H), 1.28 (s, 18 H), 1.25 (m, 8 H), 1.23 (s, 18 H), 0.84 (m, 3 H). ^{13}C NMR (100 M, $\mathrm{CDCl_3}$, TMS), δ 166.0, 164.4, 163.3, 159.4, 158.0, 156.5, 156.3, 155.7, 152.9, 152.6, 152.1, 147.4, 147.3, 140.2, 135.8, 132.9, 132.7, 131.8, 128.7, 127.6, 127.4, 126.7, 126.6, 126.2, 122.7, 121.6, 121.4, 120.4, 119.9, 119.8, 119.6, 119.4, 119.2, 119.1, 119.0, 118.3, 117.1, 113.1, 109.8, 40.7, 40.6, 39.5, 34.3, 34.2, 31.7, 31.4, 31.3, 29.2, 29.1, 28.1, 27.1, 22.6, 14.0. IR spectrum (KBr) ν = 3351, 3062, 2959, 2865, 1698, 1662, 1589, 1503, 1411, 1347, 1286, 1216, 1173, 1112, 1019, 836, 754, 554 cm^{-1}. UV−vis (CHCl$_3$): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 593 (44320), 553 (27280), 459 (16480), 293 (67670). Fluorescence (CHCl$_3$): λ_{max}/nm = 617.6, fluorescence quantum yield (λ_{exe} = 550 nm, E_{550nm} = 0.0414/1 cm, CHCl$_3$, reference TPPI with Φ = 0.96) = 0.81. MALDI-TOF calcd 1493.8, obsd 1492.7. Anal. Calcd for $C_{95}H_{92}N_6O_{11}$: C, 76.38; H, 6.21; N, 5.63. Found: C, 76.19; H, 6.17; N, 5.69.

Ligand Derivative 4c. 4-[3,5-Bis(2-hydroxyphenyl)-1,2,4-triazol-1-yl] benzoyl chloride (0.2 mmol) and *N*-octyl-*N*′-(4-aminophenyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic diimide (**3c**) (119 mg, 0.10 mmol) were allowed to react according to the general procedure except in THF and purified by column separation (silica gel, CH$_2$Cl$_2$) to yield a black powder (49 mg, 32%). ^{1}H NMR (400 M, CDCl$_3$, TMS), δ 8.24 (s, 2 H), 8.22 (s, 2 H), 8.12 (s, 1 H), 8.10 (dd, 1 H, *J* = 7.8 Hz, 1.5 Hz), 8.06 (d, 2 H, *J* = 8.5 Hz), 7.79 (d, 2 H, *J* = 8.7 Hz), 7.61 (d, 2 H, *J* = 8.5 Hz), 7.32 (m, 2 H), 7.25−7.20 (m, 10 H), 7.12 (d, 1 H, *J* = 8.3 Hz), 7.0 (m, 2 H), 6.93 (dd, 1 H, *J* = 6.0 Hz, 1.4 Hz), 6.86 (m, 8 H), 6.66 (t, 1 H, *J* = 7.2 Hz), 4.11 (t, 2 H, *J* = 7.7 Hz), 1.66 (m, 2 H), 1.34 (m, 2 H), 1.29 (s, 20 H), 1.25 (s, 24 H), 0.85 (m, 3 H). ^{13}C NMR (100 M, CDCl$_3$, TMS), δ 164.5, 163.8, 163.7, 163.4, 159.5, 158.0, 156.3, 156.1, 155.9, 152.8, 152.2, 147.4, 140.6, 138.0, 136.3, 133.0, 131.6, 131.5, 129.2, 129.0, 127.6, 127.5, 126.7, 126.7, 126.4, 122.7, 122.1, 120.3, 120.1, 119.8, 119.7, 119.3, 119.1, 118.4, 116.9, 112.9, 109.9, 34.3, 31.8, 31.5, 31.2, 29.3, 29.1, 28.1, 27.1, 22.6, 14.1. IR spectrum (KBr) ν = 3293, 3061, 2958, 2863, 1702, 1665, 1589, 1505, 1409, 1343, 1285, 1211, 1173, 1108, 1015, 831, 754, 554 cm^{-1}. UV−vis (CHCl$_3$): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 589 (41160), 548 (24820), 459 (13320), 296 (75060). Fluorescence (CHCl$_3$): λ_{max}/nm = 614.4, fluorescence quantum yield (λ_{exe} = 550 nm, $E_{550\ nm}$ = 0.0460/1 cm, CHCl$_3$, reference TPPI with Φ = 0.96) = 0.88. MALDI-TOF calcd 1541.8, obsd 1540.6. Anal. Calcd for $C_{99}\ H_{92}N_6O_{11}$: C, 77.12; H, 6.01; N, 5.45. Found: C, 76.98; H, 6.09; N, 5.61.

Ligand Derivative 7a. 4-[3,5-Bis(2-hydroxyphenyl)-1,2,4-triazol-1-yl] benzoyl chloride (0.4 mmol) and *N*,*N*′-di(8-amino-octyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic diimide (**6a**) (123 mg, 0.10 mmol) were allowed to react according to the general procedure and purified by column separation (silica gel, CH$_2$Cl$_2$/CH$_3$OH 10:1) to yield a black powder (78 mg, 40%). ^{1}H NMR (300 M, CDCl$_3$, TMS), δ 11.5 (sb, 2 H), 9.57 (sb, 2 H), 8.21 (s, 4 H), 8.12 (d, 2 H, *J* = 7.6 Hz), 7.93 (d, 4 H, *J* = 8.3 Hz), 7.57 (d, 4 H, *J* = 8.4 Hz), 7.32 (m, 4 H), 7.22 (d, 8 H, *J* = 8.7 Hz), 7.12 (d, 2 H, *J* = 8.3 Hz), 7.05 (m, 4 H), 6.91 (d, 2 H, *J* = 7.7 Hz), 6.80 (d, 8 H, *J* = 8.7 Hz), 6.64 (t, 2 H, *J* = 7.6 Hz, 7.7 Hz), 6.20 (t, 2 H, *J* = 5.0 Hz, 5.1 Hz), 4.11 (m, 4 H), 3.47 (m, 4 H), 1.65 (m, 8 H), 1.36 (m, 16 H), 1.28 (s, 36 H). ^{13}C NMR (100 M, CDCl$_3$, TMS), δ 166.1, 163.4, 159.5, 157.9, 156.4, 155.9, 152.9, 152.0, 147.3, 140.2, 136.3, 132.9, 132.8, 131.8, 128.6, 127.6, 127.6, 126.6, 126.1, 122.4, 120.5, 119.8, 119.4, 119.3, 119.1, 118.3, 117.1, 113.1, 110.0, 0.6, 40.4, 34.4, 31.5, 29.5, 29.1, 27.9, 27.0, 26.9. IR spectrum (KBr) ν = 3288, 3062, 2957, 28608, 1696, 1657, 1588, 1503, 1463, 1410.3, 1351, 1286, 1214, 1170, 1109, 1015, 835, 754, 554 cm^{-1}. UV−vis (CHCl$_3$): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 585 (46650), 545 (28030), 454 (17100). Fluorescence (CHCl$_3$): λ_{max}/nm = 614.4, fluorescence quantum yield (λ_{exe} = 5 50 nm, E_{550nm} = 0.0414/1 cm, CHCl$_3$, reference TPPI with Φ = 0.96) = 0.88. MALDI-TOF calcd 1948.3, obsd 1948.6. Anal. Calcd for $C_{122}\ H_{118}N_{10}O_{14}$: C, 75.21; H, 6.10; N, 7.19. Found: C, 74.75; H, 5.94; N, 7.21.

Ligand Derivative 7b. 4-[3,5-Bis(2-hydroxyphenyl)-1,2,4-triazol-1-yl] benzoyl chloride (0.4 mmol) and *N*,*N*′-di(2-amino-ethyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic diimide (**6b**) (107 mg, 0.10 mmol) were allowed to react according to the general procedure and purified by column separation (silica gel, CH$_2$Cl$_2$/CH$_3$OH 50:1) to yield a black powder (64 mg, 36%). ^{1}H NMR (400 M, CDCl$_3$, TMS), δ 9.61(sb, 2 H), 8.23 (s, 4 H), 8.12 (m, 2 H), 7.88 (d, 4 H, *J* = 8.4 Hz), 7.57 (s, 1 H), 7.49 (d, 4 H, *J* = 8.4 Hz), 7.38 (m, 2 H), 7.22 (m, 2 H), 7.17 (d, 8 H, *J* = 8.6 Hz), 7.15∼6.99 (m, 8 H), 6.85 (m, 2 H), 6.77 (d, 8 H, *J* = 8.7 Hz), 6.56 (t, 2 H, *J* = 7.7 Hz), 4.51 (m, 4 H), 3.87 (m, 4 H), 1.22 (s, 36 H). ^{13}C NMR (100 M, CDCl$_3$, TMS), δ 166.1, 164.2, 159.4, 158.0, 156.4, 156.0, 152.7, 152.0, 147.5, 140.2, 135.8, 132.9, 132.8, 131.8, 128.7, 127.6, 127.4, 126.7, 126.1, 121.9, 120.8, 120.2, 119.8, 119.4, 119.2, 119.0, 118.3, 117.1, 113.1, 109.8, 40.4, 39.6, 34.3, 31.5. IR spectrum (KBr) ν = 3301, 3060, 2960, 2868, 1699, 1662, 1588, 1503, 1464, 1410, 1348, 1288, 1215, 1173, 1111, 1016, 835, 753, 553 cm^{-1}. UV−vis (CHCl$_3$): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 589 (47900), 548 (28840), 457 (17900), 288 (59970). Fluorescence (CHCl$_3$): λ_{max}/nm = 620.3, fluorescence quantum yield (λ_{exe} = 550 nm, E_{550nm} = 0.0369/1 cm, CHCl$_3$, reference TPPI with Φ = 0.96) = 0.75. MALDI-TOF calcd 1779.9, obsd 1778.9. Anal. Calcd for $C_{110}\ H_{94}N_{10}O_{14}$: C, 74.22; H, 5.32; N, 7.87. Found: C, 74.02; H, 5.28; N, 7.59.

Ligand Derivative 7c. 4-[3,5-Bis(2-hydroxyphenyl)-1,2,4-triazol-1-yl] benzoyl chloride (0.4 mmol) and *N*,*N*′-di(4-amino-phenyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic diimide (**6c**) (116 mg, 0.10 mmol) were allowed to react according to the general procedure except in THF and purified by column separation (silica gel, CH$_2$Cl$_2$) to yield a black powder (56 mg, 30%). ^{1}H NMR (400 M, d_6-DMSO, TMS), δ 10.80(s, 2 H), 10.49 (s, 2 H), 10.10 (s, 2 H), 8.08∼8.04 (m, 8 H), 7.93 (s, 4 H), 7.86 (d, 4 H, *J* = 8.56 Hz), 7.61 (d, 4 H, *J* = 8.56 Hz), 7.56 (d, 4 H, *J* = 7.76 Hz), 7.43∼7.37 (m, 4 H), 7.32∼7.28 (m, 8 H), 7.05∼7.00 (m, 6 H), 6.91∼6.84 (m, 10 H), 1.23 (s, 36 H). ^{13}C NMR could not be recorded because of the low solubility of the compound; IR spectrum (KBr) ν = 3306, 3063, 1706, 1672, 1589, 1509, 1465, 1408, 1341, 1289, 1209, 1175, 1102, 802, 755, 556 cm^{-1}. UV−vis (CHCl$_3$): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 587 (51060), 546 (30640), 456 (17400), 289 (75050). Fluorescence (CHCl$_3$): λ_{max}/nm = 615.2, fluorescence quantum yield (λ_{exe} = 550 nm, E_{550nm} = 0.0343/1 cm, CHCl$_3$, reference TPPI with Φ = 0.96) = 0.90. MALDI-TOF calcd 1876.1, obsd 1874.5. Anal. Calcd for $C_{118}H_{94}N_{10}O_{14}$: C, 75.54; H, 5.05; N, 7.47. Found: C, 75.43; H, 5.12; N, 7.55.

4a + Fe + 4a. UV−vis (CHCl$_3$): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 585 (93000), 545 (56100), 454 (34000). IR spectrum (KBr) ν = 2959, 2861, 1697, 1659, 1590, 1504, 1462, 1438, 1411, 1350, 1287, 1216, 1172, 1110, 1016, 843, 755, 554 cm^{-1}. MALDI-TOF: 3207.5[**4a** + Fe + **4a**]$^-$, 1631.6[**4a** + Fe]$^-$, 1577.8[**4a**]$^-$.

4b + Fe + 4b. UV−vis (CHCl$_3$): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 589 (89100), 548 (54000), 458 (32000). IR spectrum (KBr) ν = 2959, 2865, 1697, 1661, 1589, 1503, 1463, 1435, 1410, 1346, 1287, 1216, 1172, 1111, 1016, 838, 754, 553 cm^{-1}. MALDI-TOF: 3039.1[**4b** + Fe + **4b**]$^-$, 1547.7[**4b** + Fe]$^-$, 1493.8[**4b**]$^-$.

4c + Fe + 4c. UV−vis (CHCl$_3$): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 587 (90300), 545 (56000), 457 (314000). IR spectrum (KBr) ν = 2958, 2864, 1701, 1664, 1591, 1506, 1462, 1408, 1342, 1284, 1212, 1172, 1108, 1015, 834, 755, 553 cm^{-1}. MALDI-TOF: 3135.4[**4c** + Fe + **4c**]$^-$, 1594.5[**4c** + Fe]$^-$, 1540.6[**4c**]$^-$.

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Supporting Information Available: General experimental methods and spectral data (^{1}HNMR,^{13}CNMR) for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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