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Photonic Logic Gates Based on Control of FRET by a Solvatochromic Perylene Bisimide

Yongjun Li, Haiyan Zheng, Yuliang Li,* Shu Wang, Ziyu Wu, Peng Liu, Zengqiang Gao, Huibiao Liu, and Daoben Zhu

CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China, Graduate School of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100080, People's Republic of China, and Synchrotron Radiation Laboratory, Institute of High Energy Physics, Chinese Academy of Science, Beijing 100039, People's Republic of China

ylli@iccas.ac.cn

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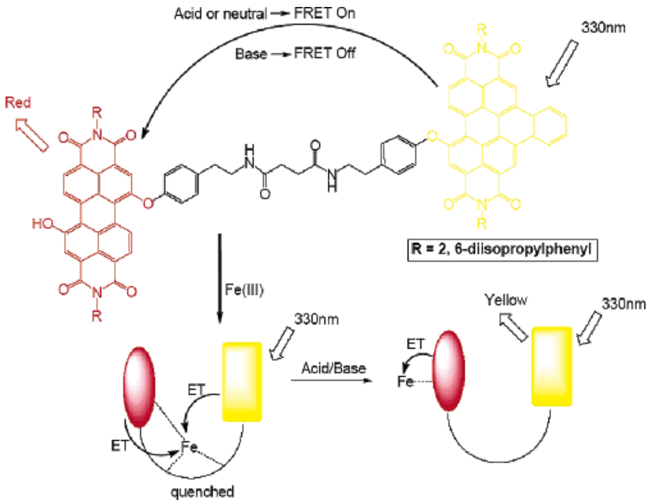

New perylenebisimide derivatives hydroxyperylenebisimide and naphthoperylenebisimide were obtained and applied to construct a new solvatochromic dyad **9**. The solvatochromic behavior of hydroxyperylenebisimide was studied, and the structure of naphthoperylenebisimide was determined by X-ray crystallography. The spectral studies indicated that the hydroxyperylenebisimide and naphthoperylenebisimide units of dyad **9** were strongly coupled in the ground state, and as a result the fluorescence of the naphthoperylenebisimide unit was almost quenched and that of the hydroxyperylenebisimide unit was greatly enhanced due to the fluorescence resonance energy transfer (FRET). As we expected, this FRET process could be tuned with the addition of protons, base, and ferric ions. This behavior of dyad **9** could be interpreted by a two-input INH logic gate, while in the presence of Fe(III), the ion complex of **9** could execute a two-input XOR logic gate. By changing the output signal, a combinational logic circuit with three inputs could also be interpreted.

Introduction

Boolean functions at the molecular scale have been demonstrated through detectable spectroscopic changes upon an ionic, electronic, photonic, or thermal input[1] and have led to the interpretation of complex molecular logic gates such as AND,[2] XOR,[3] and INHIBIT[4] functions. Several logic functions can be integrated within a single molecule by generating multiple light signals[2b,5] or by altering their chemical input.[6] On the basis of input signal multiplicity, a single molecular platform integrating multiple recognition sites for each input is expected to respond in parallel to a variety of reagents and thereby provide a range of Boolean functions.[7]

The design of organic fluorescence logic gate has provided important contributions to the development of Boolean functions.[8] Solvatochromic fluorophores are especially useful for

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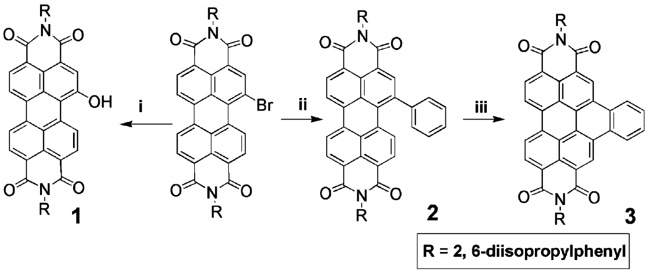
SCHEME 1. Synthesis of 1 and 3[a]



[a] Conditions: (i) H_2O, K_2CO_3, KI, DMF; (ii) phenylboronic acid, K_2CO_3, $Pd(PPh_3)_4$, toluene, ethanol; (iii) CH_2Cl_2, $h\nu$.

these purposes since they usually cover a broad range of emission wavelengths which are dependent on external stimuli.[9] Our goal is to develop systems which are operated by integrating two independent output fluorescent channels via electron transfer and/or energy transfers modulated by the solvatochromic properties of fluorophores.

Results and Discussion

With these thoughts in mind, we synthesized new perylenebisimide dyes **1** and **3** (Scheme 1), and incorporated them into a dyad **9** (Scheme 2) and initiated studies of the photoinduced electron transfer and fluorescence resonance energy transfer (FRET) processes in this newly well-defined dyad under the influence of external stimulations. In this paper, we will present the photo physic properties studies of the new dyad **9**. The results showed that metal cations and H^+/OH^- could switch the FRET between the two units in dyad **9** and that **9** could also act as a fluorescent logic gate with multiply configurable dual outputs.[10]

1-Hydroxyperylenebisimide **1** was synthesized by heating the solution of *N*,*N'*-di-(2,6-diisopropylphenyl)-1-bromoperylene-3,4:9,10-tetracarboxylic acid bisimide in DMF, in the presence of K_2CO_3, KI, and trace water. Compound **3** was obtained by photocyclization of the phenyl-subtituted perylene diimide (**2**).[11] One of the bromo moieties of 1,7-di-bromoperylenebisimide[12] was substituted by *N*-(tert-butoxycarbonyl) tyramine to obtain **4**. Subsequently compound **5** was prepared by coupling a phenyl group to **4** through a Suzuki reaction. Compound **6** was obtained with photocyclization reaction in high yield. After deprotection in acidic conditions, the resulting free amino group was coupled with succinic anhydride to give **7**. Compound **8** was obtained with the same procedure used for compound **1**. Compound **8** was deprotected and coupled with **7** to give the naphthoperylenebisimide-hydroxyperylenebisimide dyad **9**.

All the compounds were fully characterized by NMR, MS, and IR spectra. They were highly soluble in common solvents. The molecular structure of **3** was determined by X-ray crystallographic analysis, as shown in Figure 1. The most prominent feature of the structure of **3** was the perpendicular orientation of the 2,6-diisopropylphenyl groups with respect to the naphthoperylenebisimide chromophoric unit. This lead to fully isolated chromophores. In the given crystal structure three molecules of chloroform were intercalated to solvate the dye or fill the empty space created by the conformationally restricted dye molecules.[13]

For dyes **1** the solvatochromic properties were investigated in several solvents with different polarity and a significant bathochromic shift of the absorption was noted in the proton acceptor solvents (Figure 2). And we noted that the hydrogen bond played more important role than polarity in this case. In proton-acceptor solvents such as acetone, DMF, and pyridine, there were significant red shifts of the longest wavelength absorption bands. For dye **1** the absorption maximum varied from 542 nm in $CHCl_3$ to 777 nm in pyridine, this positive solvatochromic shift (235 nm) was larger than that of an aminobenzodifuranone derivative (ABF) that exhibits the largest positive solvatochromic shift in terms of wavelength shift (206 nm).[14] Similar to that aminobenzodifuranone derivative, the hydrogen-bond formation had more important influence on the electronic absorption spectrum, which was attributed to the H-bond *donating* ability of −OH.[14b] The spectra shape was like that of the perylene nucleus substituted with NR_2 groups.[15] A similar band appeared also for intramolecular proton transfer between the hydroxyl and amine substituents of aminoalkylnaphthol.[16] Addition of amines such as TEA to solutions of **9** in chloroform or THF led to the appearance of a new, low-energy absorption band, which could be considered as the extreme condition of the solvatochromisim (Figure S2), and we would also use this condition for further studies.

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(1) For examples, see: (a) Raymo, F. M.; Giordani, S. *J. Am. Chem. Soc.* **2001**, *123*, 4651−4652. (b) Raymo, F. M.; Alvarado, R. J.; Giordani, S.; Cejas, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 2361−2364. (c) Tian, H.; Qin, B.; Yao, R.-X.; Zhao, X.-L.; Yang, S.-J. *Adv. Mater.* **2003**, *15*, 2104−2107. (d) Collier, C. P.; Wong, E. W.; Belohradsky, M.; Raymo, F. M.; Stoddart, J. F.; Kuekes, P. J.; Williams, R. S.; Heath, J. R. *Science* **1999**, *285*, 391−394. (e) Collier, C. P.; Belohradsky, M.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 5831−5840. (f) Stojanovic, M. N.; Stefanovic, D. *Nat. Biotechnol.* **2003**, *21*, 1069−1074. (g) Okamoto, A.; Tanaka, K.; Saito, I. *J. Am. Chem. Soc.* **2004**, *126*, 9458−9463.

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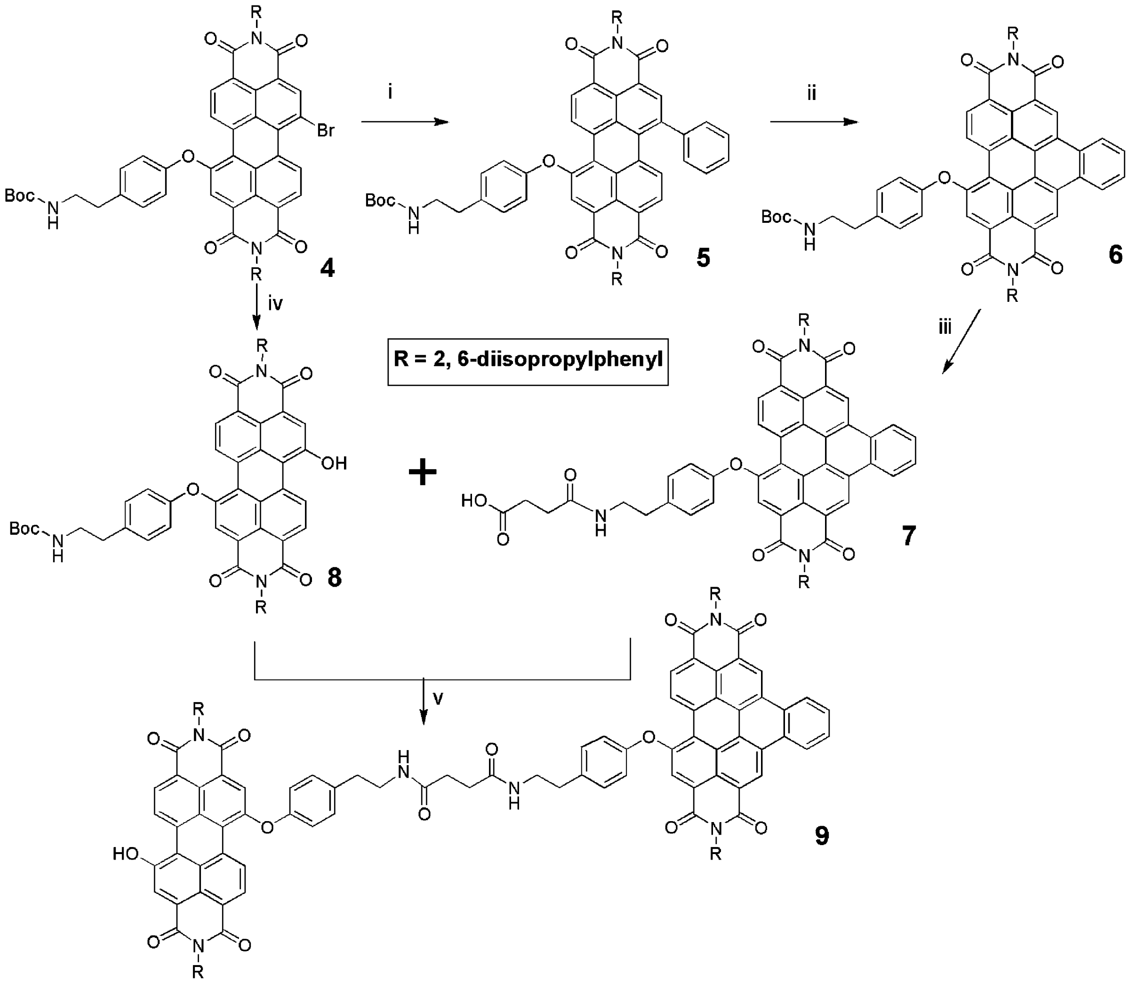
SCHEME 2. Synthesis of the Dyad 9[a]



[a] Conditions: (i) phenylboronic acid, K_2CO_3, $Pd(PPh_3)_4$, toluene, ethanol; (ii) CH_2Cl_2, $h\nu$; (iii) TFA, $CHCl_3$, then succinic anhydride, Et_3N (TEA), CH_2Cl_2; (iv) H_2O, K_2CO_3, KI, DMF; (v) TFA, $CHCl_3$, then **7**, DMAP, EDCI·HCl, CH_2Cl_2.

Figure 3a showed the UV−visible spectra of **9** as compared with the spectra of the parent **6** and **8**. Compound **9** showed superposition features of a typical naphthoperylenebisimide and hydroxyperylenebisimide moieties. The absorption patterns allowed the virtually selective excitation of naphthoperylenebisimide moiety in **9** due to the specific band of naphthoperylenebisimide at 330 nm.

Figure 3 showed a strong overlap of the emission spectrum of dye **6** with the absorption spectrum of dye **8**. According to Förster's theory,[17] long-range through-space resonance energy transfer is expected if such an overlap of the absorption and emission spectra (together with some other features such as high fluorescent quantum yields[17]) of the involved chromophores occurs. Both **9** and **8** exhibited an emission maximum at 579 nm with a shoulder at 620 nm, typical of the hydroxyperylenebisimide moiety. For compound **9** containing two chromophores, i.e., the hydroxyperylenebisimide and the naphthoperylenebisimide units, an emission from the naphthoperylenebisimide moiety between 500 and 540 nm could be expected. However, compound **9** displayed almost completely quenched naphthoperylenebisimide emission in this wavelength region and a strong and enhanced emission of hydroxyperylenebisimide compared with **8**.

On the basis of the structural properties (bulky imide substituents) and the excellent additivity of the absorption bands of the two chromophoric subunits (Figure 3a) we can exclude the possibility of intramolecular aggregation due to folding of the flexible alkyl spacer. Such aggregation would lead to strong coupling of the two dyes and open alternative through-bond mechanisms of energy transfer.[13,17] In addition intermolecular FRET processes between different molecules can be ruled out at the applied concentrations of our study because no energy transfer became apparent for equimolar mixtures of dyes **6** and **8** (Figure S1).

Figure 4 showed the absorption spectra of dyad **9** in THF under different experimental conditions. Addition of acid alone had no influence on the absorption of **9**. In the presence of TEA, the absorption peak assigned to hydroxyperylenebisimide moiety decreased and a new broad peak around 700 nm appeared. Adding Fe(III) to the solution of **9** led to an absorption enhancement in the range of 350−450 nm and without evident influence on the main bands. With the combination of Fe(III) and TEA, the absorption peak of hydroxyperylenebisimide moiety also decreased and accompanied with a new broad peak around 650 nm, which was mainly due to the influence of the

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[17] (a) Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7−17. (b) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, California, 1991; p 296.

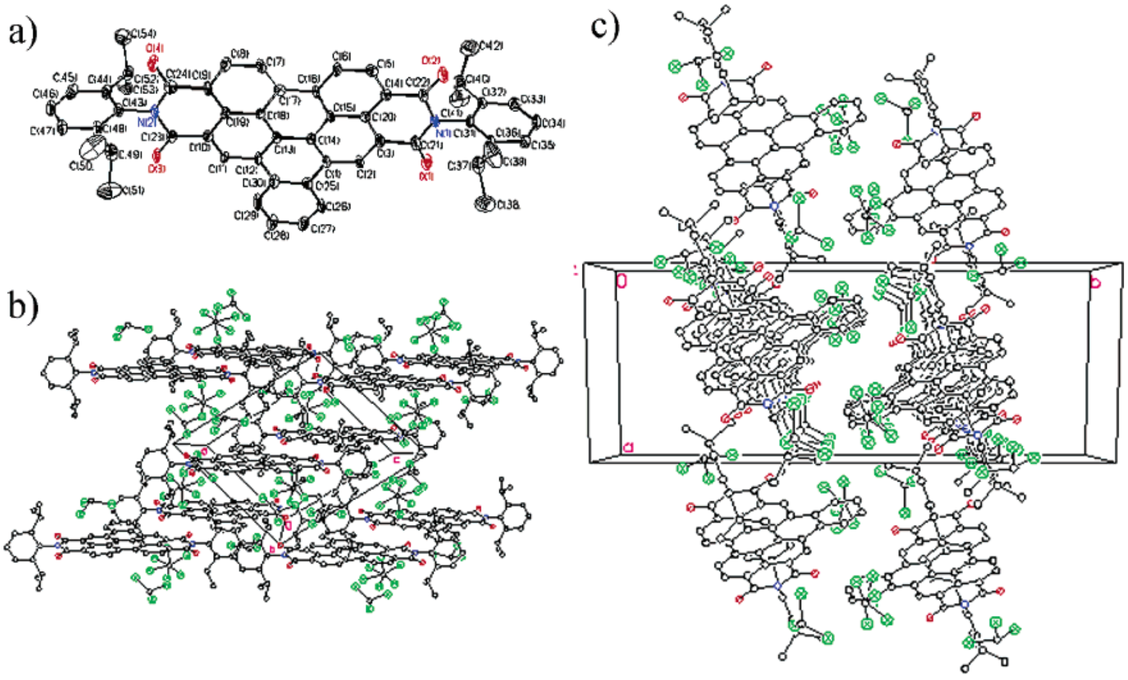

FIGURE 1. (a) X-ray crystal structure of **3**. (b) Projection of the X-ray crystal structure of **3** along the *b* axis. (c) Projection of the X-ray crystal structure of **3** along the *c* axis.

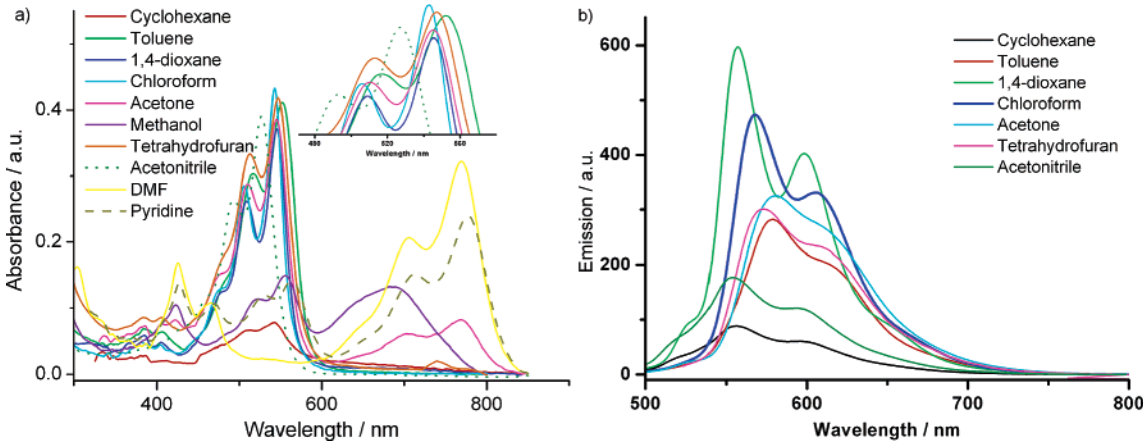

FIGURE 2. Absorption (1.1×10^{-5} M) and fluorescence spectra (1.1×10^{-6} M) of **1** in different solvents.

TEA when compared with these spectra of **9** treated with Fe(III) and other combination conditions. That is, due to the solvatochromisim of the hydroxyperylenebisimide, the absorption band of hydroxyperylenebisimide varied from 560 nm at neutral or in the presence of H^+ to 700 nm in the presence of base such as TEA (Figure 4, Figure S2−3). Thus the FRET between naphthoperylenebisimide and hydroxyperylenebisimide can be switched in the surroundings of base and acid. Upon excitation of the naphthoperylenebisimide moiety (330 nm) the molecule can switch between three distinct fluorescent states with emission of yellow, red, or off luminescence as described below (Figure 5). In the presence of TEA, the FRET was switched off; the red emission of the hydroxyperylenebisimide was replaced by the moderately enhanced yellow emission of naphthoperylenebisimide (Figure S4). Upon additon of acid, the FRET was switched on and the red emission of hydroxyperylenebisimide was regained.

Addition of iron(III) resulted in efficient fluorescent quenching[18] by the bound metal ion due to the electron transfer from naphthoperylenebisimide and hydroxyperylenebisimide to Fe(III)[19] (Figure S5). The succinamide between the two components combined with the hydroxyl group of hydroxyperylene bisimide probably form a siderophore-like Fe complex,[18a] because we did not observe the same fluorescent quenching phenomena when the separate components **6** and **8** were treated

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[18] (a) Weizman, H.; Ardon, O.; Mester, B.; Libman, J.; Dwir, O.; Hadar, Y.; Chen, Y.; Shanzer, A. *J. Am. Chem. Soc.* **1996**, *118*, 12368−12375. (b) Bodenant, B.; Fages, F.; Delville, M.-H. *J. Am. Chem. Soc*. **1998**, *120*, 7511−7519. (c) Nudelman, R.; Ardon, O.; Hadar, Y.; Chen, Y.; Libman, J.; Shanzer, A. *J. Med. Chem*. **1998**, *41*, 1671−1678.

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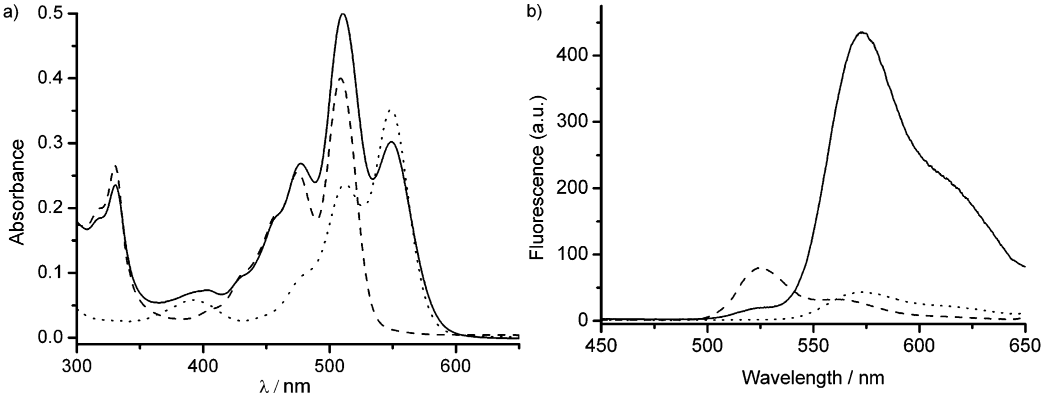

FIGURE 3. (a) Absorption spectra of **6** (dashed line), **8** (dotted line), and **9** (solid line) (1.2×10^{-5} M) in THF. (b) Fluorescence spectra of **6** (dashed line), **8** (dotted line), and **9** (solid line) (1.2×10^{-6} M) in THF; excitation at 330 nm.

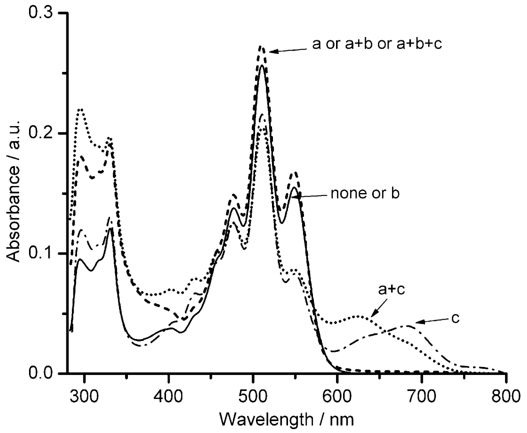

FIGURE 4. Absorption spectra of 5×10^{-6} M **9** in THF under different experimental conditions. Input: 20 μL THF solution of (a) 1 M Fe $(ClO_4)_3$, (b) 1 M TFA, and (c) 1 M TEA.

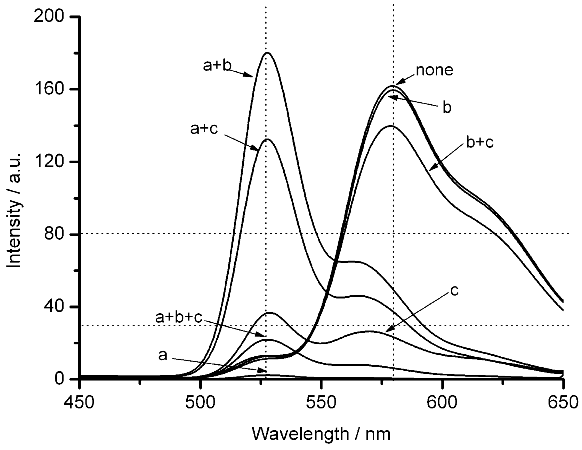

FIGURE 5. Fluorescence spectra of 5×10^{-6} M **9** in THF excited at 330 nm under different experimental conditions. Input: 20 μL THF solution of (a) 1M Fe $(ClO_4)_3$, (b) 1 M TFA, and (c) 1 M TEA.

with Fe(III). And when we treated the more concentrated **9** in THF with iron (III), there was some precipitates formed and the absorption intensity of the solution decreased. And when EDTA was added into the solution containing the precipitate, the precipitate disappeared and the absorption intensity of the solution was regained. With the addition of TEA or TFA, the yellow emission of naphthoperylenebisimide was regained.

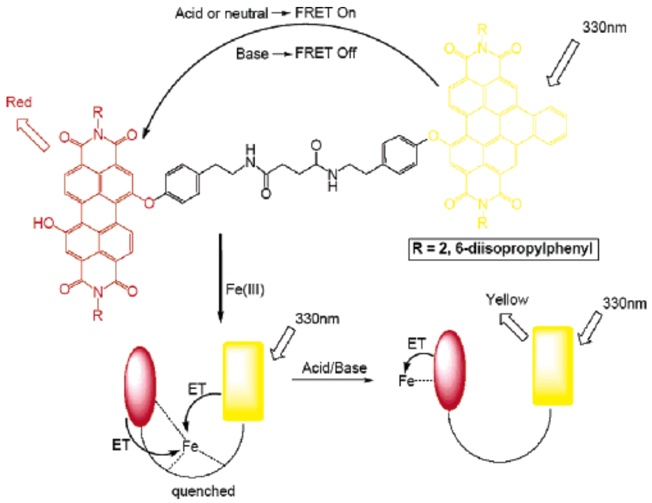

FIGURE 6. Schematic presentation describing the tune of FRET process between hydroxyperylenebisimide and naphthoperylenebisimide units of dyad **9** with the addition of TFA, TEA, and ferric ions.

When acid (TFA) was added, the pH of the system decreased, leading to protonation of the succinamide units, followed by the release of the bound metal ion from the succinamide to the hydroxyperylenebisimide, as expected from siderophore−iron(III) complexes in lower pH.[20] Since the fluorescence of the naphthoperylenebisimide was not quenched and that of hydroxyperylenebisimide was quenched by Fe(III), emission was observed predominantly at 527 nm (Figure S6). Alternatively, addition of base (TEA) to the ferric complex resulted in a yellow emission at 527 nm (Figure S7), which was due to the fact that the FRET was switched off because the absorption band of hydroxyperylenebisimide was red-shifted (as shown in Figure 4). And TEA also helped the ionization of the hydroxyperylenebisimide, so Fe(III) was easier to complex with the hydroxyperylenebisimide part. However, when both acid and base were added, a buffer solution was formed, most of the iron remained bound to the receptor, and the output signal remained essentially quenched. All these situations were summarized in the Figure 6.

From a logic viewpoint,[17,18] it could be argued that the system such as compound **9** transduced two chemical inputs (TFA and TEA) into one optical output (fluorescence emission at 527 nm)

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[20] Monzyk, B.; Crumbliss, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 4921−4929.

TABLE 1. INH Logic Gate

input 1 (TEA)	input 2 (TFA)	output[a] ($\lambda_{em} = 527$ nm)
0	0	0
0	1	0
1	0	1
1	1	0

[a] At 527 nm, the fluorescence intensity bigger than double of that of the initial solution is defined as 1, otherwise defined as 0.

TABLE 2. XOR Logic Gate

input 1 (TEA)	input 2 (TFA)	output ($\lambda_{em} = 527$ nm)
0	0	0
0	1	1
1	0	1
1	1	0

TABLE 3. Truth Table for All Possible Strings of Three Binary-Input Data and the Corresponding Output Digit (Combinational Logic Circuit Corresponding to This Truth Table Is Given in Figure 7)

input			output[a]
I1 (Fe^{3+})	I2 (TEA)	I3 (TFA)	O ($\lambda_{em} = 580$ nm)
0	0	0	1
0	0	1	1
0	1	0	0
0	1	1	1
1	0	0	0
1	0	1	0
1	1	0	0

[a] At 580 nm, the fluorescence intensity bigger than half of that of the initial solution is defined as 1, otherwise defined as 0.

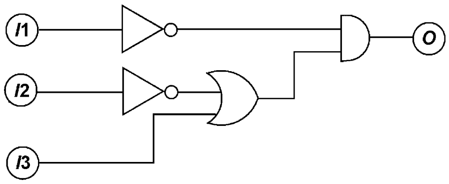

FIGURE 7. The combinational logic circuit equivalent to the truth table given in Table 3.

through an inhibit (INH) operation. In either acid or buffered solution condition, the FRET between naphthoperylenebisimide and hydroxyperylenebisimide was on and the emission at 527 nm was weak. The emission at 527 nm was relatively high only when base was added and no acid was added. If a positive logic convention (low = 0, high = 1) was applied to all signals, the signal transduction behavior of **9** translated into the truth table of a two-input INH circuit (Table 1). The output O is equal to 1 only when I1 is 1 and I2 is 0. In the presence of Fe(III), the ion complex of **9** responded to two inputs (TFA and TEA) producing one optical output (fluorescence emission at 527 nm) through a XOR operation (Table 2). When the output was defined as fluorescence emissions at 580 nm, a more complicated combinational logic circuit with three inputs (Fe^{3+}, TEA, and TFA) can be executed through a series of AND, NOT, and OR operations. The corresponding truth table was presented in Table 3, and the combinational logic circuit was shown in Figure 7.

Conclusion

In summary, the spectral studies indicated that the hydroxyperylenebisimide and naphthoperylenebisimide units of dyad **9** were strongly coupled in the ground state, and as a result the fluorescence of the naphthoperylenebisimide unit was almost quenched and that of the hydroxyperylenebisimide unit was greatly enhanced due to the FRET. However, this FRET process could be tuned with the addition of protons, base, and ferric ions. This behavior of dyad **9** could be interpreted by a two-input INH logic gate, while in the present of Fe(III), the ion complex of **9** could execute a two-input XOR logic gate. By changing the output signal, a combinational logic circuit with three inputs could also be interpreted. The results may provide a novel strategy for designing the complex photoelectronic devices, in which the system was operated by integrating two independent output fluorescent channels via electron transfer and/or energy transfers modulated by the solvatochromic properties of fluorophores.

Experimental Section

Crystallography. Single crystals of **3**, $C_{57}H_{47}N_2O_4Cl_9$ (M = 1143.02), were obtained by slow diffusion of methanol into a solution of **3** in $CHCl_3$. The unit cell was monoclinic, space group $P2_1/n$, $a = 11.064$ (2), $b = 38.215$ (8), $c = 12.976$ (3) Å, $\alpha = 90.00$, $\beta = 104.53(3)$, $\gamma = 90.00°$, $V = 5310.8(18)$Å^3, $Z = 4$, $\rho_{calcd} = 1.430$ g cm^{-3}; $R = 0.1011$(4255 data with $F_0{}^2 > 2\theta(F_0{}^2)$), and 678 refined parameters. A total of 4255 native data was collected at $T = 200$ K on a MARCCD detector at a synchrotron radiation beam line 3W1A, and the wavelength is 0.9 Å. A crystal-to-detector distance (70 mm) and an oscillation (5.0°) are necessary for getting diffraction data with higher quality. Data were processed with HKL2000. All data have been collected with the storage ring working at the energy of 2.2 GeV and with a current decreasing by about 135 mA to 80 mA during a time span of 8 h. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (SHELXTL), all non-hydrogen atoms were refined isotropically, whereby all hydrogen atoms were placed at their idealized positions.

General Method for Suzuki Coupling. *N*,*N*′-Di-(2,6-diisopropylphenyl)-1-bromoperylene-3,4:9,10-tetracarboxylic acid bisimide or *N*,*N*′-di-(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide and boronic acid were dissolved in toluene/ethanol (30 mL/10 mL), and 50 mg of K_2CO_3 was added. The solution was degassed by bubbling N_2 for 30 min. Then Pd $(PPh_3)_4$ (about 5 mg) was added. The reaction mixture was allowed to stir at 80 °C for 3 h and then reduced in volume and the resulting solid taken up with CH_2Cl_2 (50 mL) and washed with H_2O (1 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and filtered, and the solvent removed under reduced pressure to obtain a black solid, which was purified by column chromatography (CH_2Cl_2 as eluent).

General Method for Photocyclization. Compounds for cyclization (0.02−0.03 mmol) were dissolved in CH_2Cl_2 (20 mL) in a quartz vessel. The solution was directly irradiated in the sun. The progress was monitored by thin-layer chromatography (TLC). After the photocyclization was finished, the reaction mixture was concentrated under reduced pressure to afford the crude product and purified by column chromatography (CH_2Cl_2 as eluent).

1. 1 was synthesized by heating the solution of *N*,*N*′-di-(2,6-diisopropylphenyl)-1-bromoperylene-3,4:9,10-tetracarboxylic acid bisimide (32 mg, 0.04 mmol) in DMF (10 mL) at 100 °C for 10 h, in the presence of K_2CO_3 (10 equiv), KI (2 equiv), and trace water. The reaction mixture was concentrated under reduced pressure to afford the crude product and purified by column chromatography on silica with CH_2Cl_2/MeOH (20/1) to afford **1** (22 mg, yield 76%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 9.86 (d, 1 H, J= 8.4 Hz), 8.82−8.78 (m, 3 H), 8.75 (d, 1 H, J = 8.1 Hz), 8.66 (d, 1 H J = 8.0 Hz), 8.35 (s, 1 H), 7.55−7.48 (m, 2 H), 7.38−7.35 (m, 4 H), 3.41 (s, 1 H), 2.78−2.72 (m, 4 H), 1.21−1.17 (m, 24 H). HRMS calcd 727.3166 ($C_{48}H_{43}N_2O_5$, M + H), observed 727.3157.

2. *N,N′*-Di-(2,6-diisopropylphenyl)-1-bromoperylene-3,4:9,10-tetracarboxylic acid bisimide (316 mg, 0.4 mmol) and phenylboronic acid (74 mg, 0.6 mmol) reacted according to the general method to give **2** (258 mg, yield 82%). ^{1}H NMR (400 MHz, $CDCl_3$), δ ~8.80–8.68 (m, 5 H), 8.23 (d, 1 H, $J = 9$ Hz), 7.96 (d, 1 H, $J = 9$ Hz), ~7.58–7.44 (m, 7 H), ~7.35–7.26 (m, 2 H), ~2.78–2.73 (m, 4 H), ~1.26–1.14 (m, 24 H). MS TOF calcd 786.35($C_{54}H_{46}N_2O_4$), observed 786.5. Anal. calcd (%) for $C_{54}H_{46}N_2O_4$: C, 82.42; H, 5.89; N, 3.56. Found: C, 84.47; H, 5.81; N, 3.63.

3. According to general method for photocyclization, 100 mg of **2** in 100 mL CH_2Cl_2 was directly irradiated in the sun for 3 h. The reaction mixture was concentrated under reduced pressure to afford the crude product and purified by column chromatography on silica with CH_2Cl_2 to afford **3** (92 mg, yield 92%). ^{1}H NMR (300 MHz, $CDCl_3$), δ 10.34 (s, 2 H), 9.42–9.39 (m, 2 H), 9.37 (d, 2 H, $J = 8.3$ Hz), 9.16 (d, 2 H, $J = 8.1$ Hz), 8.18–8.15 (m, 2 H), 7.56 (t, 2 H, $J = 7.6$ Hz), 7.42 (d, 4 H, $J = 7.7$ Hz), 2.92–2.85 (m, 4 H), 1.26–1.22 (m, 24 H). IR: 2959, 2926, 1699, 1661, 1591, 1429, 1353, 1324, 1254, 910, 837, 728. MS TOF calcd 784.33 ($C_{54}H_{44}N_2O_4$), observed 784.6. Anal. calcd for $C_{54}H_{44}N_2O_4$: C, 82.63; H, 5.65; N, 3.57. Found: C, 82.76; H, 5.59; N, 3.49.

4. A mixture of tert-butyl-4-hydroxyphenethylcarbamate (166 mg, 0.7 mmol), anhydrous potassium carbonate (97 mg, 0.7 mmol), and 18-crown-6 (184 mg, 0.7 mmol) was stirred in toluene (50 mL) at room temperature. Then *N,N′*-di-(2,6-diisopropylphenyl)-1-bromoperylene-3,4:9,10-tetracarboxylic acid bisimide (866 mg, 1.0 mmol) was added. The reaction mixture was refluxed under nitrogen with stirring for 2 h. After cooling to room temperature, the solvent was removed by reduced pressure, and the crude product was obtained. Purification was accomplished by column chromatography on silica with CH_2Cl_2 to give **4** (510 mg, 71%): ^{1}H NMR (400 MHz, $CDCl_3$), δ 9.69–9.63 (m, 1 H), 9.49–9.44 (m, 1 H), 9.04–8.98 (m, 1 H), 8.83–8.74 (m, 2 H), 8.39–8.37 (m, 1 H), 7.52–7.46 (m, 2 H), 7.36–7.32 (m, 4 H), 7.27 (d, 2 H, $J = 8.4$ Hz), 7.11 (d, 2 H, $J = 8.4$ Hz), 4.59 (s, 1 H), 3.41–3.36 (m, 2 H), 2.83 (t, 2 H, $J = 6.8$ Hz), 2.78–2.67 (m, 4 H), 1.43 (s, 9 H), 1.19–1.14 (m, 24 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 163.5, 163.3, 163.2, 162.8, 162.6, 162.5, 155.9, 155.6, 153.5, 145.6, 138.5, 137.5, 136.2, 134.3, 133.6, 133.1, 131.9, 131.0, 130.9, 130.3, 130.3, 129.8, 129.8, 129.7, 129.7, 129.7, 129.3, 129.0, 128.8, 128.4, 128.0, 125.5, 124.6, 124.4, 124.2, 124.1, 124.0, 123.5, 123.3, 122.6, 122.5, 122.4, 122.3, 121.7, 120.4, 119.5, 119.5, 119.4, 41.8, 35.6, 29.2, 29.2, 28.4, 24.0, 23.8. IR (KBr) ν 3396, 3066, 2964, 2929, 2870, 1709, 1670, 1592, 1502, 1469, 1398, 1337, 1261, 1201, 1168, 737 cm^{-1}. MS TOF calcd 1023.35 ($C_{61}H_{58}BrN_3O_7$), observed 1023.2. Anal. calcd for $C_{61}H_{58}BrN_3O_7$: C, 71.48; H, 5.70; N, 4.10. Found: C, 71.51; H, 5.57; N, 4.08.

5. 4 (205 mg, 0.2mmol) and phenylboronic acid (69 mg, 0.5mmol) reacted according to the general Suzuki coupling method to give **5** (200 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 9.54–9.49 (m, 1 H), 8.75–8.67 (m, 2 H), 8.38 (s, 1 H), 8.22–8.16 (m, 1 H), 8.04–7.96 (m, 1 H), 7.60–7.46 (m, 7 H), 7.35–7.29 (m, 4 H), 7.27 (d, 2 H, $J = 8.4$ Hz), 7.14 (d, 2 H, $J = 8.4$ Hz), 4.67–4.51 (br, 1 H), 3.39 (m, 2 H), 2.83 (m, 2 H), 2.77–2.70 (m, 4 H), 1.43 (s, 9 H), 1.18–1.14 (m, 24 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 163.5, 163.5, 163.3,162.8,155.8, 155.3, 153.7,145.6, 145.6, 145.6, 145.5, 142.4, 141.2, 125.9, 135.8,134.8, 134.8, 133.9,133.0, 131.9, 131.7, 130.9, 130.8, 130.5, 130.3, 130.1, 129.9, 129.8, 129.6, 129.1, 128.8, 128.6, 128.5, 125.8, 124.9, 124.4, 124.2, 124.0, 123.9, 122.3, 122.1, 121.9,119.3, 119.2, 41.7, 35.6, 29.2, 29.1, 28.3, 24.1, 23.9. IR (KBr) ν 3395, 3062, 2964, 2929, 2870, 1707, 1669, 1593, 1502, 1469, 1405, 1333, 1262, 1201, 1168, 737 cm^{-1}. MS TOF calcd 1021.47 ($C_{67}H_{63}N_3O_7$), observed 1021.6. Anal. calcd for $C_{67}H_{63}N_3O_7$: C, 78.72; H, 6.21; N, 4.11. Found: C, 78.77; H, 6.17; N, 4.13.

6. 6 was gained according to general method for photocyclization (yield 90%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 10.37 (s, 1 H), 10.32 (s, 1 H), 10.31 (d, 1 H, $J = 8.5$ Hz), 9.41 (d, 2 H, $J = 5.4$ Hz), 9.12 (d, 1 H, $J = 8.5$ Hz), 8.74 (s, 1 H), 8.19–8.16 (m, 2 H), 7.58–7.53 (m, 2 H), 7.43–7.39 (m, 2 H), 7.32 (d, 2 H, $J = 8.3$ Hz), 7.24 (d, 2 H, $J = 8.3$ Hz), 4.70 (s, 1 H), 3.43 (m, 2 H), 2.92–2.85 (m, 6 H), 1.46 (s, 9 H), 1.29–1.19 (m, 24 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 171.1,164.0, 163.8, 163.7, 163.4, 156.5, 156.0, 153.6, 145.8, 136.5, 133.2, 131.1, 130.8, 130.6, 130.5, 129.8, 129.2, 129.0, 128.8, 128.4, 128.0, 127.8, 127.3, 127.2, 127.1, 126.6, 125.2, 124.7, 124.6, 124.2, 124.0, 123.7, 123.3, 122.4, 122.3, 122.1, 121.7, 119.9, 66.4, 41.9, 35.7, 29.5, 29.4, 28.5, 24.3, 24.2, 24.2, 24.1. IR (KBr) ν 3368, 3067, 2965, 2929, 2870, 1710, 1670, 1620, 1597, 1525, 1502, 1469, 1435, 1379, 1328, 1282, 1258, 1204, 1167, 745 cm^{-1}. MS TOF calcd 1019.45 ($C_{67}H_{61}N_3O_7$), observed 1019.7. Anal. calcd for $C_{67}H_{61}N_3O_7$: C, 78.88; H, 6.03; N, 4.12. Found: C, 78.91; H, 6.06; N, 4.08.

7. To a stirred solution of **6** (152 mg, 0.15 mmol) in anhydrous $CHCl_3$ (10 mL) was added TFA (2 mL). The solution was stirred until the deprotection was complete by TLC; then the solution was reduced in volume and the excess of TFA removed in vacuo. The resulting solid was taken up in anhydrous CH_2Cl_2 (50 mL), and one drop of Et_3N was added. Then a solution of succinic anhydride (50 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was added slowly over 30 min. After 16 h, the solution was reduced in volume and purification was accomplished by column chromatography on silica with CH_2Cl_2/MeOH (10/1) to give **7** (99 mg, yield 65%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 10.29 (s, 1 H), 10.27–10.25 (m, 1 H), 10.23 (s, 1 H), 9.38–9.32 (m, 2 H), 9.11 (d, 1 H, $J = 4.6$ Hz), 8.72 (s, 1 H), 8.20–8.13 (m, 2 H), 7.57–7.51 (m, 2 H), 7.42–7.37 (m, 4 H), 7.34 (d, 2 H, $J = 8.4$ Hz), 7.28 (d, 2 H, $J = 8.4$ Hz), 6.21 (s, 1 H), 3.60 (t, 2 H, $J = 6.0$ Hz), 2.92–2.86 (m, 4 H), 2.83 (t, 2 H, $J = 6.8$ Hz), 2.63 (t, 2 H, $J = 6.4$ Hz), 2.48 (t, 2 H, $J = 6.4$ Hz), 1.27–1.15 (m, 24 H). MS TOF calcd 1020.17 ($C_{66}H_{57}N_3O_8$), observed 1020.3. Anal. calcd for $C_{66}H_{57}N_3O_8$: C, 77.70; H, 5.63; N, 4.12. Found: C, 77.68; H, 5.59; N, 4.14.

8. The solution of **4** (102 mg, 0.1mmol) in DMF (10 mL) was heated at 100 °C for 10 h, in the presence of K_2CO_3 (10 equiv), KI (2 equiv), and trace water. The reaction mixture was concentrated under reduced pressure to afford the crude product and purified by column chromatography on silica with CH_2Cl_2/MeOH (20/1) to afford **8** (75 mg, yield 78%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 9.68 (d, 1 H, $J = 8.6$ Hz), 9.63 (d, 1 H, $J = 8.2$ Hz), 8.88 (s, 1 H), 8.77 (d, 1 H, $J = 8.1$ Hz), 8.62 (d, 1 H, $J = 8.6$ Hz), 8.42 (s, 1 H), 7.60–7.56 (m, 1 H), 7.52–7.46 (m, 1 H), 7.40 (d, 2 H, $J = 7.8$ Hz), 7.33 (d, 2 H, $J = 7.5$ Hz), 7.23 (d, 2 H, $J = 7.3$ Hz), 7.08 (d, 2 H, $J = 7.3$ Hz), 4.61 (s, 1 H), 3.40–3.36 (m, 2 H), 2.81–2.71 (m, 6 H), 1.43 (s, 9 H), 1.18–1.14 (m, 24 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 164.3, 163.8, 163.6, 163.3, 156.3, 156.2, 154.4, 153.9, 145.7, 145.7, 135.5, 135.3, 133.4, 130.9, 130.8, 130.5, 130.3, 129.8, 129.6, 129.5, 129.3, 128.8, 128.6, 126.1, 125.5, 125.2, 124.3, 124.1, 123.5, 123.1, 122.0, 121.0, 119.3, 119.0, 41.8, 35.5, 29.7, 29.2, 28.4, 24.0. MS TOF calcd 962.14 ($C_{61}H_{59}N_3O_8$), observed 962.1. Anal. calcd for $C_{61}H_{59}N_3O_8$: C, 76.15; H, 6.18; N, 4.37. Found: C, 76.22; H, 6.14; N, 4.39.

9. To a stirred solution of **8** (50 mg, 0.05 mmol) in anhydrous $CHCl_3$ (10 mL) was added TFA (2 mL). The solution was stirred until the deprotection was complete by TLC; then the solution was reduced in volume and the excess of TFA removed in vacuo. The resulting solid was purified by column chromatography roughly ($CHCl_3$/MeOH, 10/1). The resulting solid was taken up in anydrous CH_2Cl_2 (50 mL), and 4-DMAP (12.5 mg, 0.1 mmol), **7** (61 mg, 0.06 mmol), and EDCI•HCl (19.5 mg, 0.1 mmol) were added sequentially under cooling with an ice bath. And the solution was allowed to stir for 16 h. The reaction mixture was washed with a saturated solution of citric acid (3 × 20 mL) and H_2O (3 × 20 mL). The organic layer was dried over anhydrous $MgSO_4$ and filtrated, and the filtrate reduced in volume and the resulting solid purified by chromatography on silica gel using a gradient of CH_2Cl_2 to CH_2Cl_2/MeOH (20/1) to obtain the desired compound as a red powder (**9**, 42 mg, 45%, there are some product that coupled with the hydroxyl group of compound **8**, which was separated during the chromatography). ^{1}H NMR (400 MHz, $CDCl_3$), δ 10.30

(s, 1 H), 10.22 (d, 1 H, $J = 8.5$ Hz), 10.16 (s, 1 H), 9.66 (d, 1 H, $J = 8.3$ Hz), 9.45 (d, 1 H, $J = 8.1$ Hz), 9.40−9.34 (m, 1 H), 9.34−9.26 (m, 1 H), 9.06 (d, 1 H, $J = 8.6$ Hz), 8.78 (s, 1 H), 8.67 (s, 1 H), 8.62 (d, 1 H, $J = 8.0$ Hz), 8.47 (d, 1 H, $J = 8.1$ Hz), 8.30 (s, 1 H), 8.13−8.06 (m, 2 H), 7.57−7.51 (m, 2 H), 7.42−7.34 (m, 6 H), 7.33−7.28 (m, 4 H), 7.24−7.17 (m, 8 H), 7.00 (d, 2 H, $J = 7.8$ Hz), 6.87 (br, 2 H), 3.50−3.41 (m, 4 H), 2.91−2.83 (m, 4 H), 2.75−2.60 (m, 8 H), 2.58−2.45 (m, 4 H), 1.26−1.05 (m, 48 H). MS TOF calcd 1862.7 ($C_{122}H_{106}N_6O_{13}$), observed 1885.6 (M + Na), 1901.7 (M + K). Anal. calcd for $C_{122}H_{106}N_6O_{13}$: C, 78.60; H, 5.73; N, 4.51. Found: C, 78.63; H, 5.75; N, 4.53.

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Supporting Information Available: NMR spectral data, UV−vis and fluoresce titration spectra of the dyad **9.** This material is available free of charge via the Internet at http://pubs.acs.org.

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