Electronic Supplementary Information

For

Asymmetric dinuclear bis(dipyrrinato)zinc(II) complexes: Broad absorption and unidirectional quantitative exciton transmission

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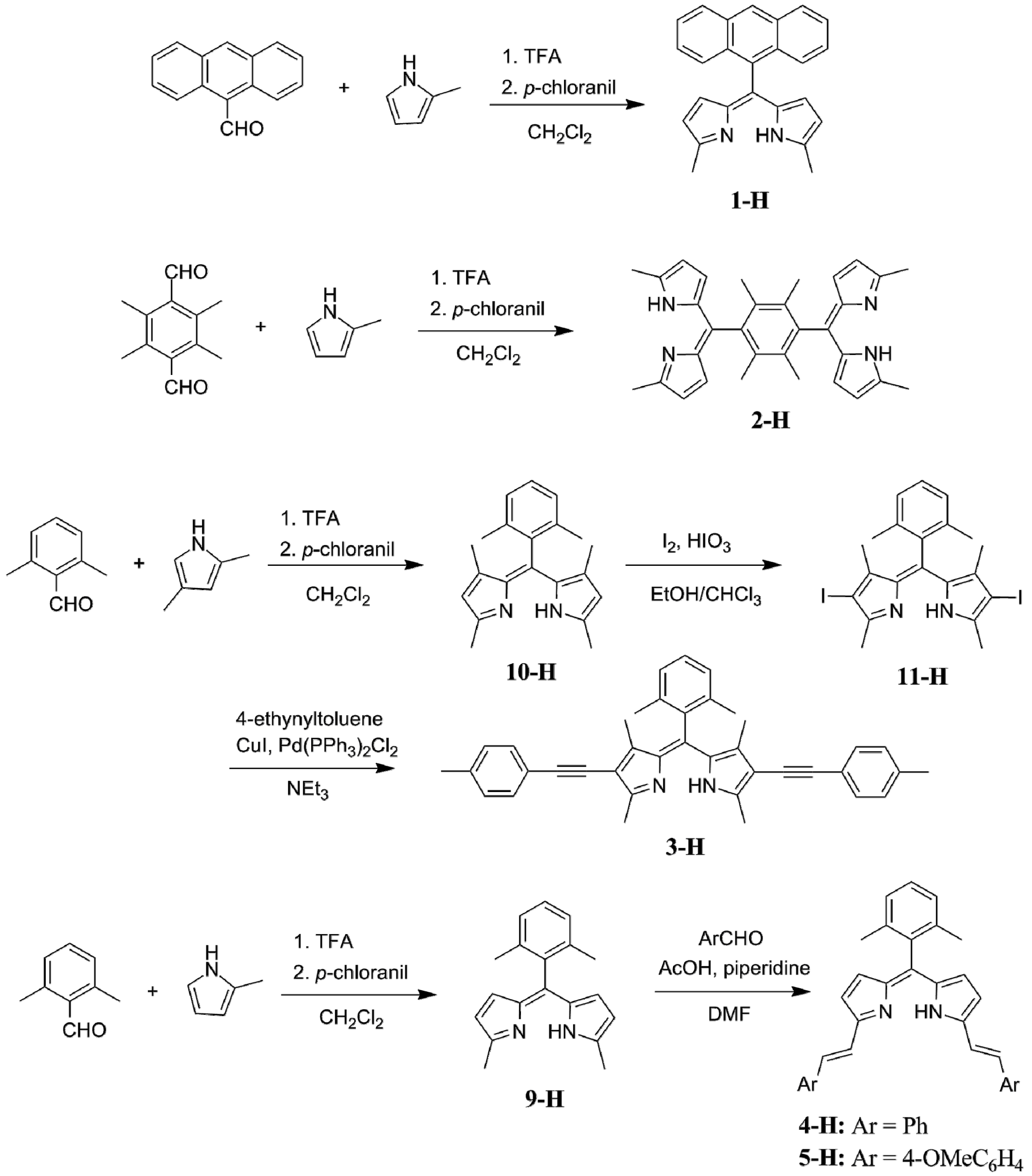
1. General experimental procedure

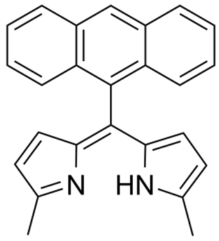
All chemicals were purchased from Tokyo Chemical Industry Co., Ltd., Kanto Chemical Co., or Wako Pure Chemical Industries, Ltd. and used without further purification. Dipyrrinato ligands were prepared according to **Scheme 1**.Preparative gel permeation liquid chromatography was performed by LC-918 with JAIGEL 1-H + 2-H columns (Japan Analytical Industry) with chloroform as the solvent. ^{1}H NMR and ^{13}C NMR data were collected in $CDCl_3$ or CH_2Cl_2 on a Bruker DRX 500 spectrometer. Tetramethylsilane (δ_H = 0.00) was used as an internal standard for the ^{1}H NMR spectra, and $CDCl_3$ (δ_C = 77.00) was used as an interrnal standard for the ^{13}C NMR spectra, respectively. High resolution mass spectroscopy was performed on either of a JEOL JMS-700MStation mass spectrometer (HRFAB-MS) or a Waters LCT Premier XE spectrometer (HRESI-MS). UV-vis absorption spectra were recorded with a JASCO V-570 spectrometer. Steady-state fluorescence spectra were collected with a HITACHI F-4500 spectrometer. Absolute photo luminescent quantum yields were collected with a Hamamatsu Photonics C9920-02G. Fluorescence lifetime measurements were performed using a Hamamatsu Photonics Quantaurus-Tau C11367-02.



Scheme S1 Synthesis of dipyrrinato ligands.

2. Synthesis

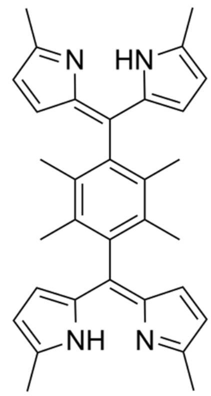
2.1 terminal dipyrrin 1-H[1]



To a dichloromethane solution (20 mL) of 9-anthracenecarboxaldehyde (0.501 g, 2.4 mmol) and 2-methylpyrrole (0.43 mL, 50 mmol), was added trifluoroacetic acid (10 μL) and stirred overnight at room temperature. *p*-chloranil (0.603 g, 2.4 mmol)was added and stirred another 2 h. The reaction mixture was processed by column chromatography (alumina, dichloromethane) and recrstallisation (methanol/dichloromethane) to give the pure product as a brown powder (0.407 g, 48 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.52 (s, 1H), 8.02 (d, J = 8.6 Hz, 2H), 7.92 (m, J = 8.6 Hz, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.34 (t, J = 7.8 Hz, 2H), 5.99 (d, J = 4.2 Hz, 2H), 5.87 (d, J = 4.2 Hz, 2H), 2.48 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=153.85, 141.14, 134.49, 131.14, 131.11, 130.88, 128.59, 128.09, 127.36, 126.87, 125.80, 125.15, 117.89, 16.38 ; HRFAB-MS: 349.1687 [M+H]$^+$, calcd. for: $C_{25}H_{21}N_2^+$: 349.1699.

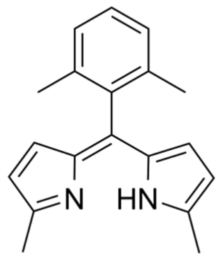
2.2 bridging dipyrrin 2-H



To a dichloromethane solution (40 mL) of 2,6-dimethylbenzaldehyde (0.378 g, 2.0 mmol) and 2-methylpyrrole (0.70 mL, 8.4 mmol), was added trifluoroacetic acid (20 μL) and stirred overnight at room temperature. *p*-chloranil (0.978 mg, 4.0 mmol) was added and stirred 90 min. The desired product was purified by column chromatography (alumina, dichloromethane) followed by recrystallisation from methanol/dichloromethane as a brown powder (0.231 mg, 24%).

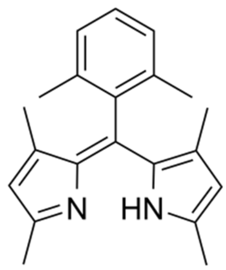
^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.27 (d, J = 3.9 Hz, 4H), 6.13 (d, J = 3.9 Hz, 4H), 2.46 (s, 12H), 2.06 (s, 12H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.51, 139.76, 138.27, 136.03, 132.32, 127.68, 117.39, 17.47, 16.37; HRFAB-MS: 475.2845 $[M+H]^+$, calcd. for: $C_{32}H_{35}N_4^+$: 475.2856.

2.3 dipyrrin 9-H



To a dichloromethane solution (40 mL) of 2,6-dimethylbenzaldehyde (0.608 g, 4.4 mmol) and 2-methylpyrrole (1.04 mL, 10 mmol), was added trifluoroacetic acid (25 μL) and stirred overnight at room temperature. *p*-chloranil (1.09 g, 4.4 mmol)was added and stirred another 90 min. The reaction mixture was processed by column chromatography (alumina, 20% dichloromethane/hexane) and recrstallisation (hexane/dichloromethane) to give the pure product as a brown powder (0.756 g, 56 %).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 7.6 Hz, 2H), 6.23 (d, J = 4.2 Hz, 2H), 6.09 (t, J = 4.2 Hz, 2H), 6.09 (t, J = 4.2 Hz, 2H), 2.44 (s, 6H), 2.14 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.58, 139.23, 136.92, 136.59, 136.43, 127.55, 127.38, 126.80, 117.49, 19.92, 16.31; HRFAB-MS: 277.1697 $[M+H]^+$, calcd. for: $C_{19}H_{21}N_2^+$: 277.1699.

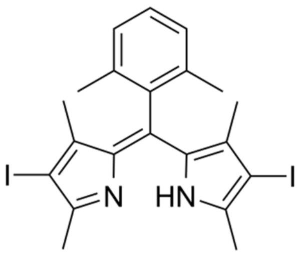
2.4 dipyrrin 10-H[2]



To a dichloromethane solution (40 mL) of 2,6-dimethylbenzaldehyde (688 mg, 5.0 mmol) and 2,4-dimethylpyrrole (1.08 mL, 10.2 mmol), was added trifluoroacetic acid (20 μL) and stirred overnight at room temperature. *p*-chloranil (1.23 g, 5.0 mmol) was added and stirred another 90 min. The reaction mixture was processed by column chromatography (alumina, 10% dichloromethane/hexane) to give the pure product as a brown powder (1.11 g, 73 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.6 Hz, 2H), 5.86 (s, 2H), 2.35 (s, 6H), 2.15 (s, 6H), 1.27 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.23, 139.48, 137.27, 136.88, 135.94, 135.09, 127.97, 127.72, 119.06, 19.62, 16.08, 13.48; HRFAB-MS: 305.2011 $[M+H]^+$, calcd. for: $C_{21}H_{25}N_2^+$: 305.2018.

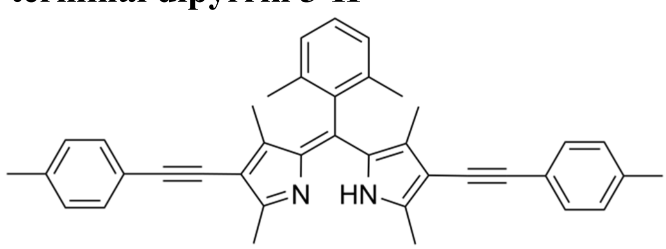
2.5 π-extended terminal dipyrrin 11-H[2]



To a chloroform/ethanol = 1:1 solution (40 mL) of **10-H** (304 mg, 1.0 mmol) and iodine (508 mg, 2.0 mmol), an aqueous solution (3 mL) of iodic acid (352 mg, 2.0 mmol) was added and stirred 1 h at room temperature. The solution was diluted with chloroform (100 mL) and the organic layer was washed with an aqueous solution of sodium sulfite (5%, 100 mL). The organic layer was dried over sodium sulfate and evaporated to give the pure product as a brown powder (437 mg, 79%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 7.6 Hz, 2H), 2.41 (s, 6H), 2.10 (s, 6H), 1.27 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.02, 141.25, 137.27, 136.38, 135.77, 135.19, 128.57, 128.04, 83.25, 19.65, 17.13, 15.56; HRFAB-MS: 556.9933 $[M+H]^+$, calcd. for: $C_{21}H_{23}I_2N_2^+$: 556.9945.

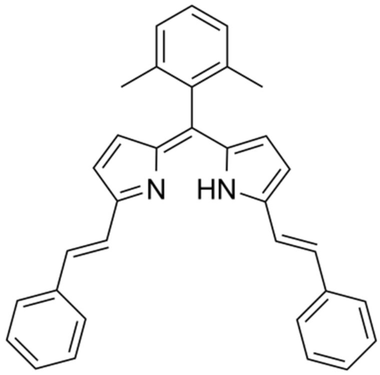
2.6 π-extended terminal dipyrrin 3-H[2]



A triethylamine solution (30 mL) of **11-H** (370 mg, 6.7 mmol), 4-ethynyltoluene (260 μL, 21 mmol), copper(I) iodide (7 mg, 3.7 x 10^{-2} mmol), and bis(triphenylphosphine)palladium(II) dichloride (23 mg, 3.3 x 10^{-2} mmol) was heated to 70 °C and stirred overnight at room temperature. Alumina was added to the reaction mixture and the solution was dried *in vacuo*. The residue was processed by column chromatography (alumina, 100% hexane then 33% dichloromethane/hexane) and recrstallisation (hexane/dichloromethane) to give the pure product as a red powder (183 mg, 52 %).

All spectral data were consistent with literature previously reported[2a].

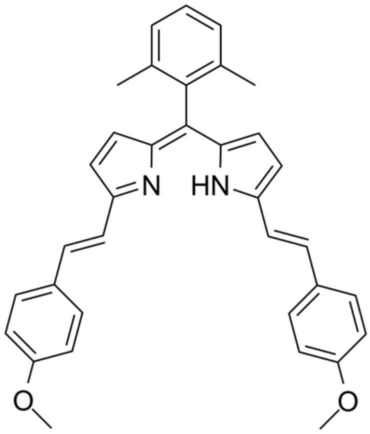
2.7 π-extended terminal dipyrrin 4-H[3]



To a N,N-dimethylformamide solution (15 mL) of acetic acid (0.5 mL) and piperidine (0.5 mL), were added 2-Medipyrrin (284 mg, 1.0 mmol) and benzaldehyde (0.63 mL, 6.0 mmol) and heated to reflux for 3 h. After cooling the solution, the solution was diluted with a mixture of ethyl acetate/hexane = 1:1 and washed with distilled water. The organic layer was dried over Na_2SO_4 and evaporated. The dark purple solid was recrystallized from hexane/dichloromethane to give **4-H** as a black solid (360 mg, 80 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58 (d, J = 7.3 Hz, 4H), 7.41 (t, J = 7.6 Hz, 4H), 7.32 (t, J = 7.3 Hz, 2H), 7.28-7.20 (m, 5H), 7.12 (d, J = 7.8 Hz, 2H), 6.62 (d, J = 4.4 Hz, 2H), 6.38 (d, J = 4.4 Hz, 2H), 2.18 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.28, 141.76, 137.08, 136.85, 136.31, 136.20, 132.42, 128.80, 128.25, 127.97, 127.85, 126.99, 126.84, 121.10, 117.29, 20.07; HRFAB-MS: 453.2329 $[M+H]^+$, calcd. for: $C_{33}H_{30}N_2^+$: 453.2325.

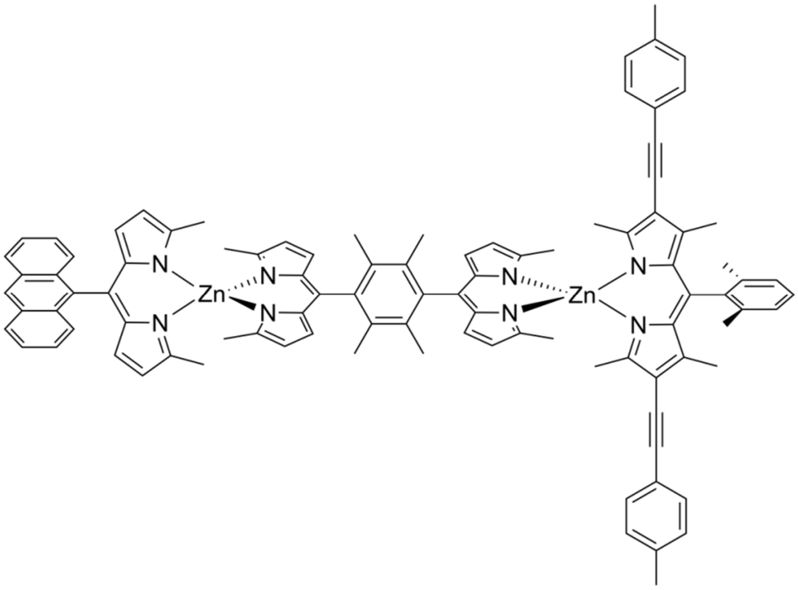
2.8 π-extended terminal dipyrrin 5-H[3]



To a N,N-dimethylformamide solution (10 mL) of acetic acid (0.5 mL) and piperidine (0.5 mL), were added 2-Medipyrrin (284 mg, 1.0 mmol) and 4-methoxybenzaldehyde (1.0 mL, 8.0 mmol) and heated to reflux for 2 h. After cooling the solution, the solution was diluted with ethyl acetate and washed with distilled water twice. The organic layer was dried over Na_2SO_4 and evaporated. The dark purple solid was recrystallized from hexane/dichloromethane to give **5-H** as a black solid (459 mg, 90 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52 (d, J = 8.8 Hz, 4H), 7.24-7.20 (m, 3H), 7.12-7.07 (m, 4H), 6.95 (d, J = 8.8 Hz, 2H), 6.58 (d, J = 4.2 Hz, 2H), 6.35 (d, J = 4.25 Hz, 2H), 3.86 (s, 6H), 2.17 (s, 6H), ; ^{13}C NMR (125 MHz, $CDCl_3$): δ =159.78, 153.41, 141.65, 137.13, 136.34, 135.52, 131.91, 129.74, 128.16, 127.73, 127.71, 126.94, 119.12, 116.93, 114.25, 55.32, 20.05 ; HRFAB-MS: 513.2543 $[M+H]^+$, calcd. for: $C_{35}H_{34}O_2N_2^+$: 513.2537.

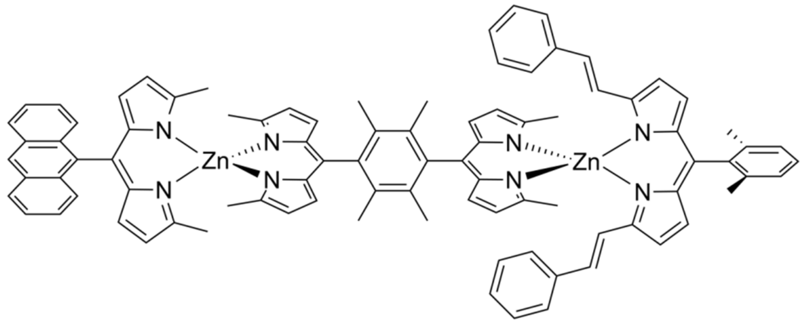
2.9 dinuclear complex 6



To a chloroform solution (20 mL) of zinc acetate (74 mg, 0.20 mmol, 2 eq.) and triethylamine (200 μL), was added a chloroform solution (6 mL) of **2-H** (94 mg, 0.10 mmol, 1eq.) dropwise and stirred 2 min, followed by addition of a chloroform solution (6 mL) of **1-H** (70 mg, 0.10 mmol, 1eq) and **3-H** (106mg, 0.10 mmol, 1eq). The solution was stirred overnight at room temperature and evaporated. The residue was filtered by Millipore twice and processed with GPC to isolate the crude product. **6** was obtained as a brown-black solid (8 mg, 3 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ=8.55 (s, 1H), 8.06 (d, J = 8.6 Hz, 2H), 7.97 (d, J = 8.8 Hz, 2H), 7.47 (t, J = 7.1 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.32-7.26 (m, 5H), 7.18 (d, J = 7.6 Hz, 2H), 7.10 (d, J = 8.1 Hz, 4H), 6.58 (d, J = 3.9 Hz, 2H), 6.56 (d, J = 3.9 Hz, 2H), 6.28 (d, J = 3.9 Hz, 2H), 6.22 (d, J = 3.9 Hz, 2H), 6.07 (d, J = 4.2 Hz, 4H), 2.38 (s, 6H), 2.33 (s, 6H), 2.26 (s, 6H), 2.21 (s, 6H), 2.19 (s, 6H), 2.18 (s, 6H), 2.17 (s, 6H), 2.15 (s, 6H), 1.47 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 159.14, 159.07, 158.65, 158.61, 144.99, 144.88, 144.83, 144.50, 140.89, 140.20, 138.96, 138.79, 138.40, 137.87, 137.79, 137.55, 135.73, 134.62, 133.13, 132.76, 132.14, 132.12, 131.71, 131.67, 131.39, 130.94, 130.86, 129.00, 128.46, 128.29, 128.13, 127.20, 127.01, 125.83, 125.12, 121.02, 117.58, 117.09, 117.04, 114.32, 95.77, 83.35, 21.45, 19.36, 17.39, 17.33, 16.83, 16.60, 16.56, 15.38, 13.70 ; HRESI-MS: 1458.5558 $[M+H]^+$, calcd. for: $C_{96}H_{87}N_8Zn_2^+$: 1458.5558.

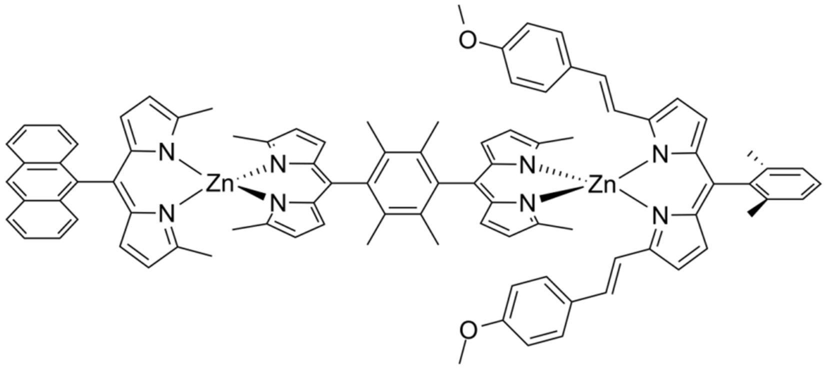
2.10 dinuclear complex 7



To a chloroform solution (20 mL) of zinc acetate (74 mg, 0.20 mmol, 2 eq.) and triethylamine (200 μL), was added a chloroform solution (6 mL) of **2-H** (94 mg, 0.10 mmol, 1eq.) dropwise and stirred 2 min, followed by addition of a chloroform solution (6 mL) of **1-H** (70 mg, 0.10 mmol, 1eq) and **4-H** (90 mg, 0.10 mmol, 1eq). The solution was stirred overnight at room temperature and evaporated. The residue was filtered by Millipore twice and processed with GPC to isolate the crude product. **7** was obtained as a brown-black solid (6 mg, 2%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.55 (s, 1H), 8.06 (d, J = 8.6 Hz, 2H), 7.98 (d, J = 8.8 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.28 (t, J = 7.6 Hz, 1H), 7.21-7.16 (m, 14H), 7.00 (d, J = 16.1 Hz, 2H), 6.84 (d, J = 4.2 Hz, 2H), 6.63 (d, J = 3.9 Hz, 2H), 6.60 (d, J = 3.9 Hz, 2H), 6.57 (d, J = 4.4 Hz, 2H), 6.30 (d, J = 3.9 Hz, 4H), 6.26 (d, J = 3.7 Hz, 2H), 6.08 (d, J = 3.9 Hz, 2H), 6.06 (d, J = 3.9 Hz, 6H), 2.39 (s, 6H), 2.24 (s, 6H), 2.23 (s, 6H), 2.22 (s, 6H), 2.09 (s, 6H), 1.96 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 159.14, 159.13, 158.66, 158.47, 145.10, 145.05, 141.70, 141.11, 140.91, 140.21, 139.13, 138.98, 138.55, 137.80, 137.58, 137.03, 136.91, 133.12, 132.97, 132.79, 132.40, 132.11, 132.03, 131.63, 131.49, 131.39, 130.87, 128.41, 128.14, 127.92, 127.65, 127.23, 127.05, 127.01, 126.96, 125.84, 125.12, 122.21, 117.59, 117.55, 117.05, 115.07, 20.02, 18.05, 17.38, 16.84, 16.78, 16.61; HRESI-MS: 1398.4933 [M+H]$^+$, calcd. for: $C_{90}H_{79}N_8O_2Zn_2^+$: 1398.4932.

2.11 dinuclear complex 8



To a chloroform solution (20 mL) of zinc acetate (74 mg, 0.20 mmol, 2 eq.) and triethylamine (200 μL), was added a chloroform solution (6 mL) of **2-H** (94 mg, 0.10

mmol, 1eq.) dropwise and stirred 2 min, followed by addition of a chloroform solution (6 mL) of **1-H** (70 mg, 0.10 mmol, 1eq) and **5-H** (102 mg, 0.10 mmol, 1eq). The solution was stirred overnight at room temperature and evaporated. The residue was filtered by Millipore twice and processed with GPC to isolate the crude product. **8** was obtained as a brown-black solid (6 mg, 2%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.55 (s, 1H), 8.06 (d, *J* = 8.6 Hz, 2H), 7.97 (d, *J* = 8.6 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 6.4 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 4H), 7.09 (d, *J* = 16.1 Hz, 2H), 6.87 (d, *J* = 16.1 Hz, 2H), 6.80 (d, *J* = 4.2 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 3.9 Hz, 2H), 6.60 (d, *J* = 3.7 Hz, 2H), 6.54 (d, *J* = 4.2 Hz, 2H), 6.28 (d, *J* = 3.9 Hz, 2H), 6.26 (d, *J* = 3.7 Hz, 2H), 6.08 (d, *J* = 3.9 Hz, 2H), 6.06 (d, *J* = 3.9 Hz, 2H), 3.75 (s, 6H), 2.39 (s, 6H), 2.24 (s, 6H), 2.22 (s, 6H), 2.21 (s, 6H), 2.10 (s, 6H), 2.00 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.57, 159.21, 159.12, 158.67, 158.56, 144.98, 144.95, 140.91, 140.88, 140.83, 140.21, 139.11, 138.95, 138.70, 137.83, 137.66, 137.08, 133.12, 132.79, 132.42, 132.12, 131.91, 131.61, 131.39, 131.24, 130.87, 129.85, 128.38, 128.14, 127.55, 127.22, 127.01, 126.91, 125.83, 125.12, 120.30, 117.59, 117.54, 117.02, 114.69, 113.85, 83.95, 55.31, 20.01, 18.14, 17.39, 16.83, 16.77, 16.59; HRESI-MS: 1462.5132 $[M]^+$, calcd. for: $C_{92}H_{83}N_8O_2Zn_2^+$: 1462.5144.

3. DFT calculation

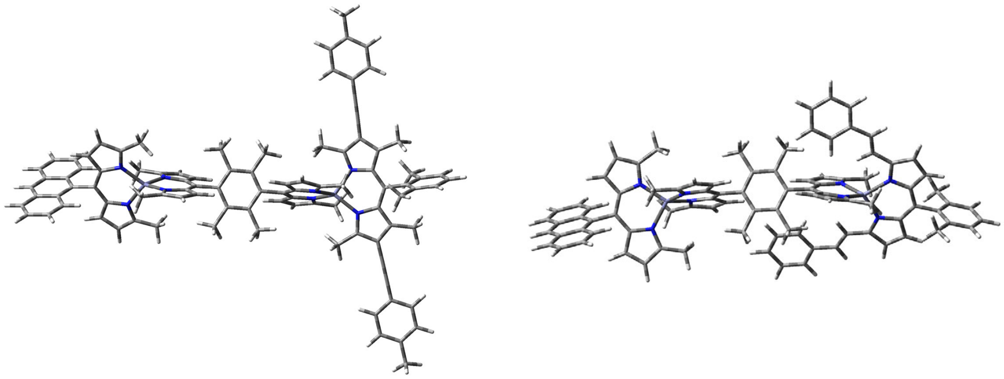


Fig. S1 Optimized structures of dinuclear complexes **6** (left) and **7** (right).

Optimized structures of dinuclear complexes **6** and **7** are shown in Fig. S1, and their coordinates are assembled in Tables S1 and S2. DFT calculation was performed at the B3LYP-D/6-31G* level under the SCRF(solvent=toluene) effect. The dipyrrin moieties around the zinc centres are not perpendicular to each other; they have distorted tetrahedral geometries. Overall, the complexes display low degrees of symmetry.

Table. S1 Cartesian coordinates (in Å) of the optimized complex **6**.

Atom	X	Y	Z	Atom	X	Y	Z
Zn	-5.235	-0.221	0.223	C	-0.561	2.293	0.583
Zn	7.175	0.047	-0.556	H	-1.562	2.028	0.929
N	-6.831	-1.360	0.066	H	-0.046	2.822	1.393
C	-8.157	-0.895	0.085	H	-0.676	3.004	-0.247
C	-9.034	-2.031	0.044	C	2.319	2.465	0.319
C	-8.203	-3.160	0.004	H	3.345	2.467	-0.055
N	-6.269	1.444	0.503	H	1.778	3.294	-0.152
C	-6.744	3.653	0.368	H	2.359	2.676	1.397
C	-7.961	2.976	0.204	C	7.621	0.086	2.752
C	-7.647	1.576	0.283	H	8.076	-0.910	2.654
C	-8.508	0.472	0.132	H	8.224	0.777	2.152
C	-9.961	0.788	-0.025	H	7.678	0.386	3.805
C	-10.502	0.891	-1.318	C	7.270	0.109	-3.927
C	-10.759	0.981	1.114	H	8.001	0.650	-3.316
C	-11.861	1.194	-1.456	H	7.631	-0.925	-4.030
C	-12.115	1.277	0.944	H	7.239	0.552	-4.928
C	-12.666	1.385	-0.333	C	2.490	-2.462	-0.941
H	-12.284	1.279	-2.454	H	2.462	-2.658	-2.022
H	-12.739	1.423	1.823	H	3.539	-2.372	-0.648
H	-13.721	1.617	-0.453	H	2.068	-3.341	-0.441
C	-10.159	0.865	2.494	C	0.223	1.072	0.153
H	-9.673	-0.111	2.627	C	-1.920	-0.209	-0.064
H	-9.385	1.628	2.650	C	-2.451	-0.788	1.103
H	-10.926	0.983	3.267	C	-1.712	-1.365	2.175
C	-9.628	0.685	-2.531	N	-3.811	-0.890	1.402
H	-8.776	1.376	-2.523	C	-2.633	-1.817	3.106
H	-9.212	-0.330	-2.544	C	-3.918	-1.501	2.593
H	-10.196	0.841	-3.454	C	-2.638	0.327	-1.141
C	-5.733	2.658	0.547	C	-2.101	1.031	-2.262
C	-6.856	-2.689	0.010	N	-4.028	0.327	-1.247
C	-4.265	2.883	0.702	C	-4.350	1.010	-2.352
H	-3.812	2.085	1.301	C	-5.257	-1.781	3.200
H	-3.768	2.877	-0.277	H	-5.913	-0.904	3.121
H	-4.073	3.852	1.175	H	-5.764	-2.605	2.679
C	-9.268	3.679	-0.015	H	-5.158	-2.054	4.256
H	-9.745	3.376	-0.953	C	-5.780	1.262	-2.718
H	-9.989	3.462	0.781	H	-6.414	0.416	-2.428
H	-9.093	4.760	-0.043	H	-6.164	2.147	-2.189
C	-5.616	-3.518	-0.070	H	-5.887	1.436	-3.794
H	-5.236	-3.549	-1.102	H	-2.438	-2.311	4.050
H	-4.824	-3.100	0.559	C	-3.177	1.465	-3.017
H	-5.829	-4.547	0.238	H	-3.156	2.035	-3.937
C	-10.531	-2.118	0.067	C	4.648	0.197	-3.917
H	-10.957	-1.625	0.948	H	4.479	0.248	-4.985
H	-10.986	-1.637	-0.806	C	5.015	-0.102	3.036
H	-10.827	-3.172	0.079	H	4.969	-0.210	4.112
C	-6.522	5.046	0.367	H	2.625	0.202	-2.997
C	-6.312	6.246	0.366	H	2.907	-0.211	2.341

C	-8.590	-4.516	-0.029	H	-1.047	1.188	-2.448
C	-8.910	-5.692	-0.053	H	-0.633	-1.425	2.219
C	-6.068	7.647	0.364	N	8.755	1.194	-0.852
C	-7.126	8.564	0.195	C	10.061	0.800	-0.547
C	-4.763	8.153	0.537	C	8.818	2.444	-1.338
C	-6.879	9.934	0.198	C	10.162	2.900	-1.372
H	-8.137	8.189	0.068	H	10.488	3.871	-1.724
C	-4.532	9.526	0.537	N	8.216	-1.555	-0.016
H	-3.939	7.459	0.673	C	7.730	-2.711	0.455
C	-5.582	10.440	0.365	C	9.584	-1.537	0.247
H	-7.708	10.628	0.071	C	8.773	-3.495	1.026
H	-3.520	9.899	0.676	C	9.938	-2.762	0.892
C	-9.283	-7.064	-0.081	H	8.652	-4.475	1.470
C	-8.303	-8.079	-0.105	C	6.265	-3.014	0.401
C	-10.642	-7.444	-0.080	H	5.740	-2.540	1.242
C	-8.676	-9.420	-0.128	H	5.820	-2.616	-0.519
H	-7.253	-7.801	-0.100	H	6.085	-4.094	0.446
C	-10.998	-8.790	-0.103	C	7.580	3.189	-1.729
H	-11.407	-6.674	-0.056	H	6.796	2.496	-2.052
C	-10.026	-9.800	-0.131	H	7.184	3.767	-0.881
H	-7.907	-10.189	-0.141	H	7.790	3.896	-2.540
H	-12.050	-9.065	-0.097	C	10.428	-0.451	-0.022
C	-5.319	11.926	0.335	C	11.876	-0.632	0.323
H	-5.098	12.268	-0.686	C	12.305	-0.393	1.644
H	-6.190	12.491	0.688	C	12.788	-1.041	-0.670
H	-4.458	12.190	0.962	C	13.700	-0.572	1.980
C	-10.421	-11.256	-0.188	C	11.407	0.025	2.678
H	-10.536	-11.593	-1.229	C	14.181	-1.216	-0.325
H	-9.661	-11.892	0.280	C	12.388	-1.297	-2.022
H	-11.378	-11.427	0.318	C	14.125	-0.329	3.324
C	1.623	1.149	0.046	C	14.599	-0.978	0.989
C	-0.425	-0.137	-0.152	C	11.856	0.249	3.954
C	0.299	-1.279	-0.534	H	10.359	0.158	2.436
C	1.703	-1.217	-0.589	C	15.099	-1.632	-1.339
C	2.350	0.000	-0.312	C	13.301	-1.695	-2.964
C	3.845	0.070	-0.386	H	11.344	-1.168	-2.289
C	4.530	0.070	0.837	C	13.233	0.069	4.284
C	3.963	-0.101	2.136	H	15.177	-0.469	3.563
N	5.912	0.183	0.970	H	15.648	-1.111	1.245
C	6.203	0.073	2.272	H	11.159	0.566	4.724
C	4.412	0.109	-1.672	H	16.144	-1.759	-1.065
C	3.702	0.171	-2.906	C	14.676	-1.865	-2.621
N	5.781	0.094	-1.951	H	12.978	-1.884	-3.984
C	5.918	0.142	-3.286	H	13.568	0.251	5.302
C	-0.406	-2.573	-0.876	H	15.383	-2.181	-3.383
H	0.042	-3.040	-1.760	H	10.936	-3.029	1.213
H	-0.327	-3.298	-0.053	C	10.942	1.874	-0.868
H	-1.469	-2.414	-1.073	H	12.016	1.850	-0.745

Table. S2 Cartesian coordinates (in Å) of the optimized complex **7**.

Atom	X	Y	Z	Atom	X	Y	Z
Zn	-5.895	0.299	-0.243	C	2.957	-0.639	-2.183
Zn	6.411	-0.036	0.080	N	5.050	-0.258	-1.338
N	-7.468	1.199	-1.023	C	3.879	-1.261	-3.004
C	-8.784	0.873	-0.696	C	5.160	-1.010	-2.441
C	-7.500	2.327	-1.747	C	3.898	1.272	1.018
C	-8.839	2.772	-1.918	C	3.394	2.155	2.015
H	-9.143	3.655	-2.466	N	5.256	1.058	1.259
N	-6.930	-1.069	0.744	C	5.588	1.776	2.344
C	-6.475	-2.134	1.418	C	6.487	-1.531	-2.893
C	-8.322	-1.155	0.716	H	7.289	-0.826	-2.645
C	-7.557	-2.950	1.851	H	6.718	-2.478	-2.385
C	-8.717	-2.334	1.416	H	6.491	-1.713	-3.973
H	-7.464	-3.868	2.418	C	6.989	1.803	2.868
C	-5.009	-2.367	1.619	H	7.471	0.825	2.754
H	-4.538	-2.744	0.701	H	7.596	2.529	2.312
H	-4.495	-1.432	1.876	H	7.001	2.085	3.927
H	-4.838	-3.095	2.419	H	3.686	-1.837	-3.901
C	-6.239	2.969	-2.235	C	4.458	2.481	2.839
H	-5.642	3.345	-1.394	H	4.456	3.138	3.699
H	-5.612	2.242	-2.769	C	-3.914	3.510	1.630
H	-6.461	3.802	-2.910	H	-3.913	4.432	2.198
C	-9.168	-0.232	0.081	C	-3.215	-2.330	-2.118
C	-10.639	-0.447	0.256	H	-2.993	-3.235	-2.670
C	-11.383	-1.071	-0.766	H	-1.776	3.068	1.212
C	-11.264	-0.021	1.447	H	-1.238	-1.467	-1.596
C	-12.802	-1.278	-0.586	H	2.369	2.496	2.077
C	-10.782	-1.528	-1.983	H	1.881	-0.620	-2.285
C	-12.685	-0.229	1.615	N	7.179	-1.843	0.353
C	-10.546	0.628	2.503	C	8.543	-2.094	0.389
C	-13.547	-1.919	-1.625	C	6.541	-3.034	0.391
C	-13.414	-0.852	0.597	C	8.741	-3.510	0.480
C	-11.532	-2.140	-2.954	C	7.496	-4.097	0.469
H	-9.716	-1.380	-2.126	H	9.707	-3.995	0.525
C	-13.312	0.210	2.824	H	7.262	-5.153	0.515
C	-11.186	1.036	3.644	N	8.148	0.872	-0.129
H	-9.480	0.789	2.385	C	8.368	2.194	-0.303
C	-12.934	-2.338	-2.776	C	9.769	2.467	-0.245
H	-14.614	-2.066	-1.476	C	10.397	1.256	-0.032
H	-14.483	-1.008	0.729	H	10.229	3.441	-0.356
H	-11.057	-2.480	-3.870	H	11.457	1.064	0.066
H	-14.381	0.045	2.937	C	9.374	0.257	0.047
C	-12.587	0.824	3.811	C	9.552	-1.120	0.275
H	-10.623	1.526	4.434	C	5.102	-3.099	0.314
H	-13.510	-2.824	-3.559	H	4.598	-2.139	0.269
H	-13.075	1.154	4.724	C	7.236	3.068	-0.466
H	-9.740	-2.658	1.557	H	6.278	2.559	-0.479
C	-9.647	1.858	-1.262	C	4.368	-4.235	0.261
H	-10.725	1.862	-1.175	H	4.883	-5.195	0.308
C	-0.388	1.576	-1.032	C	7.238	4.415	-0.572
C	1.680	0.830	0.002	H	8.184	4.956	-0.605
C	0.961	0.083	0.957	C	6.020	5.220	-0.665
C	-0.444	0.069	0.899	C	6.098	6.551	-1.117

C	-1.101	0.789	-0.114	C	4.753	4.709	-0.309
C	-2.593	0.690	-0.216	C	4.950	7.334	-1.245
C	-3.087	-0.401	-0.949	H	7.069	6.962	-1.380
C	-2.317	-1.430	-1.567	C	3.609	5.491	-0.439
N	-4.438	-0.681	-1.150	H	4.662	3.706	0.098
C	-4.515	-1.830	-1.835	C	3.699	6.806	-0.912
C	-3.338	1.668	0.458	H	5.032	8.356	-1.604
C	-2.825	2.815	1.132	H	2.646	5.074	-0.158
N	-4.729	1.676	0.567	C	2.914	-4.307	0.138
C	-5.072	2.769	1.265	C	2.278	-5.564	0.183
C	1.649	-0.712	2.048	C	2.105	-3.164	-0.026
H	1.579	-0.182	3.008	C	0.891	-5.675	0.079
H	1.176	-1.690	2.174	H	2.887	-6.458	0.305
H	2.708	-0.874	1.843	C	0.721	-3.274	-0.120
C	1.787	2.484	-1.929	H	2.556	-2.183	-0.088
H	2.814	2.652	-1.597	C	0.104	-4.529	-0.070
H	1.831	2.031	-2.929	H	0.426	-6.657	0.117
H	1.301	3.461	-2.038	H	0.126	-2.372	-0.222
C	-1.101	2.379	-2.097	C	10.966	-1.600	0.388
H	-2.156	2.106	-2.173	C	11.630	-1.509	1.626
H	-1.047	3.455	-1.879	C	11.611	-2.129	-0.744
H	-0.634	2.230	-3.078	C	12.953	-1.957	1.715
C	-5.837	-2.450	-2.163	C	12.935	-2.568	-0.622
H	-6.279	-2.917	-1.272	C	13.604	-2.484	0.599
H	-6.549	-1.691	-2.510	H	13.469	-1.890	2.669
H	-5.729	-3.216	-2.938	H	13.439	-2.975	-1.495
C	-6.504	3.092	1.558	H	14.632	-2.828	0.681
H	-7.024	3.444	0.657	C	10.887	-2.224	-2.067
H	-7.045	2.203	1.905	H	10.050	-2.931	-2.005
H	-6.576	3.871	2.325	H	10.462	-1.254	-2.352
C	-1.220	-0.746	1.912	H	11.565	-2.557	-2.860
H	-0.874	-0.529	2.929	C	10.928	-0.934	2.834
H	-2.292	-0.545	1.863	H	10.683	0.125	2.678
H	-1.067	-1.822	1.746	H	9.981	-1.455	3.022
C	1.016	1.610	-0.963	H	11.557	-1.017	3.727
C	3.170	0.709	-0.043	H	-0.977	-4.608	-0.151
C	3.691	-0.011	-1.131	H	2.805	7.416	-1.010

4. Fluorescence lifetime

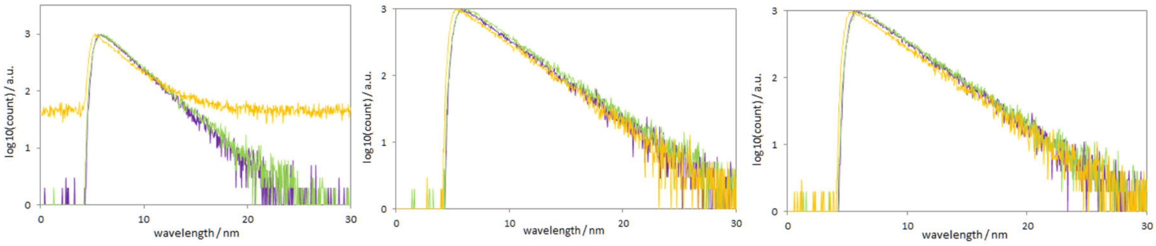


Fig. S2 Fluorescence lifetimes of complexes **6** (left), **7** (middle), and **8** (right). (Yellow line: λ_{ex} = 590 nm. Green line: λ_{ex} = 470 nm. Purple line: λ_{ex} = 365 nm.)

Fluorescence lifetime measurements at three different complexes are shown in Fig. S2. Decay curves were practically independent of the excitation wavelength. Baseline of **6** at 590 nm appears different from the rest of the decay curves because this measurement required collection of weak fluorescence (the absorptivity at 590 nm is weak in **6**), leading to enhanced noise from scattering and other sources.

5. Derivation of rate constants[4]

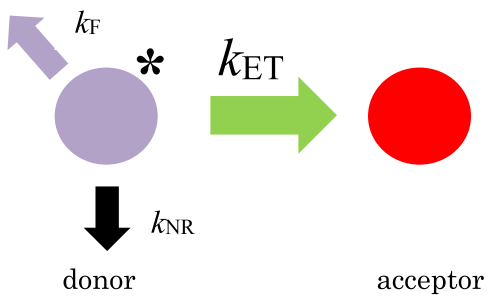


Fig. S3 Energy transfer dynamics of multiple fluorescent pigment systems.

Energy transfer dynamics of multiple fluorescent pigment systems can be briefly depicted as Fig. S3. Irradiation of the "donor" pigment generates excitons, which follow either of the following processes: emitted as fluorescence at the rate k_F or consumed by non-radiative decay processes (rate: k_{NR}). Non-radiative decay processes include energy transfer to the "acceptor" pigment (rate: k_{ET}), internal conversion, intersystem crossing, etc. (combined rate: k_{NR}', so that $k_{NR} = k_{ET} + k_{NR}$'). Rate constants k_F and k_{NR} can be derived from fluorescent quantum yield and lifetime measurements[4]. Here, k_{ET} of complex **6** is estimated.

In general, fluorescent lifetime τ of a pigment is described as:

$$\tau = 1 / (k_F + k_{NR})$$

Fluorescent quantum yield ϕ_F is described as

$$\phi_F = k_F * \tau = k_F / (k_F + k_{NR})$$

The rate constant of fluorescence emission k_F can be calculated using the formulas above as:

$$k_F = \phi_F / \tau$$

The rate constant of fluorescence emission k_{NR} can be calculated similarly:

$$k_{NR} = (1 - \phi_F) / \tau$$

When there are acceptor pigments in close proximity, excitons are dominantly consumed by energy transfer at the rate of k_{ET}. k_{NR} can be determined by measuring the fluorescence quantum yield of the donor in the donor-acceptor pigment system (ϕ_F').

Assuming k_F and k_{NR} remain constant under the presence of other pigments in close proximity, k_{ET} can be derived as

$$k_{ET} = (1 - \phi_F') \, k_F / \phi_F' - k_{NR}$$

Table S3 Rate constants of pigments.

	ϕ_F	τ / ns	k_F / s^{-1}	k_{NR} / s^{-1}
12	0.36	5.25	6.9×10^7	1.2×10^8
13	0.18	3.9	4.6×10^7	2.1×10^8
6	0.73	2.6	2.8×10^8	1.0×10^8
7	0.76	3.7	2.1×10^8	6.5×10^7
8	0.75	3.5	2.1×10^8	7.1×10^7

Based on the formulae, k_F and k_{NR} can be calculated as in Table S3. Those of anthracene (**12**) and a homoleptic bis(α,α'-dimethyldipyrrinato)zinc(II) complex using ligand **9-H** (**13**) were extracted from previous literatures.[2a,5]

Since no fluorescence was observed from the anthracene or α,α'-dimethyldipyrrin moieties, ϕ_F' was assumed to be $\phi_F' < 10^{-4}$. Under this assumption, k_{ET} of the anthracene and α,α'-dimethyldipyrrin moieties can be calculated as: k_{ET}(anthracene) > 7×10^{10} $s^{-1}$and k_{ET}(α,α'-dimethyldipyrrin) > 5×10^{10} s^{-1}. It should be noted that k_{ET}(anthracene) is the sum of the rate of energy transfer from the anthracene moiety to either of the α,α'-dimethyldipyrrin or β-arylethynyldipyrrin moieties and k_{ET}(α,α'-dimethyldipyrrin) is the rate of energy transfer from either of the α,α'-dimethyldipyrrin moieties to the β-arylethynyldipyrrin moiety.

6. References for ESI

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