Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

A new special pair model comprising *meso*-di-*p*-anisylaminoporphyrin: enhancement of visible-light absorptivities and quantification of electronic communication in mixed-valent cation radical

Ryota Sakamoto,*[ab] Michihiro Nishikawa,[b] Takeshi Yamamura,[a] Shoko Kume,[b] and Hiroshi Nishihara[b]

[a] Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3, Kagurazaka, Shinjuku-ku, Tokyo, 162-8601, Japan. Fax: (+81) 3-5228-8251; E-mail: ryota_s@rs.kagu.tus.ac.jp

[b] Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan. Fax (+81) 3-5841-4489; E-mail: sakamoto@chem.s.u-tokyo.ac.jp

Materials.

2[1], [5-bromo-10,20-di-(3,5-di-*tert*-butylphenyl)-15-triisopropylsilylethynylporphinato]zinc(II) **3**[2], and di-*p*-anisylamine[3] were prepared according to previous reports. THF for amination, toluene, and dichloromethane for electrochemistry and NIR spectroscopy were distilled over CaH_2, and pyridine over KOH pellets. Dichloromethane (spectroscopic grade, without MeOH as a stabilizer, Kanto Chemical) for UV/vis and PL spectroscopies were used as received. [D_2]dichloromethane was treated with CaH_2 to remove acidic impurities. Other materials were used as they were otherwise noted.

Synthesis of [5-di-*p*-anisylamino-10,20-di-(3,5-di-*tert*-butylphenyl)-15-triisopropylsilylethynylporphinato]zinc(II) 4.

Under an argon atmosphere, a mixture of **3** (101 mg, 0.10 mmol), di-*p*-anisylamine (84 mg, 0.36 mmol), cesium carbonate (47 mg, 0.14 mmol), palladium acetate (1.1 mg), DPEphos (4.3 mg) in THF (4 mL) was refluxed at 68°C for 43 h with shielding from light. The crude product was diluted with hexane, then filtered through celite. The filtrate was evaporated, and the resultant residue was purified with column chromatography on silica gel, eluting with a mixture of hexane and dichloromethane (2.5:1 then 2:1 v/v). A green fraction was collected, and concentrated to furnish dark-green solid of **4** (28 mg, 24%). ^{1}H NMR (600 MHz, [D_1]chloroform): δ=9.74 (d, J=4.2 Hz, 2H, β-pyrrole), 9.23 (d, J=4.2 Hz, 2H, β-pyrrole), 8.95 (d, J=4.8 Hz, 2H, β-pyrrole), 8.80 (d, J=4.8 Hz, 2H, β-pyrrole), 8.00 (d, J=1.8 Hz, 4H, 3,5-di-^{t}Bu**Ph**), 7.77 (dd, J=1.8, 1.8 Hz, 2H, 3,5-di-^{t}Bu**Ph**), 7.17 (d, J=9.0 Hz, 4H, MeO**Ph**), 6.58 (d, J=9.6 Hz, 4H, MeO**Ph**), 3.51 (s, 6H, OMe), 1.52 (s, 36H, ^{t}Bu), 1.45-1.42 (m, triisopropyl, 21H); ^{13}C NMR (150 MHz, [D_1]chloroform): δ=153.16, 152.76, 152.44, 150.42, 149.78, 148.63, 146.92, 141.17, 133.21, 133.17, 130.83, 130.66, 129.33, 124.33, 123.13, 123.11, 121.02, 114.44, 109.42, 100.43, 97.61, 55.39, 35.03, 31.75, 19.13, 11.89; HR-FAB-MS: *m/z* 1155.5764; calcd for $C_{73}H_{85}N_5O_2SiZn$, [M^+]: 1155.5764.

Synthesis of 1. Under an argon atmosphere, To **4** (71 mg, 0.061 mmol) in THF (15 mL) was added *n*Bu_4F in THF (280 μL, 0.28 mmol) at ambient temperature. The mixture was stirred for 30 min with shielding from light. Then the mixture was diluted with dichloromethane (200 mL), and washed with water (100 mL) and brine (100 mL). The organic phase was dried over Na_2SO_4, filtered through celite. The filtrate was evaporated to obtain [5-di-*p*-anisylamino-10,20-di-(3,5-di-tert-butylphenyl)-15-ethynylporphinato]zinc(II). This material was vacuumed for 1 h, then added CuCl (2.5 mg). The mixture was further vacuumed for 2 h. To the mixture were added toluene (7mL) and benzyl azide (53 μL, 0.41 mmol), and the suspension was heated at 100°C for 24 h. After evaporation of the solvent, the residue was

purified with column chromatography on silica gel, eluting with a mixture of hexane and dichloromethane (2:1 then 1:3 v/v). A green fraction was collected, and concentrated to furnish dark-purple solid of **1** (59 mg, 85%). ^{1}H NMR (600 MHz, [D_1]chloroform, as $\mathbf{1_2}$, Figure S1b): δ=9.36 (d, J=4.3 Hz, 4H, β-pyrrole), 8.78 (d, J=4.4 Hz, 4H, β-pyrrole), 8.15 (brdd, 4H, 3,5-di-^{t}Bu**Ph**), 8.07 (d, J=4.4 Hz, 4H, β-pyrrole), 7.88 (brdd, 4H, 3,5-di-^{t}Bu**Ph**), 7.85 (d, J=9.3 Hz, 4H, MeO**Ph**), 7.77 (brdd, 4H, 3,5-di-^{t}Bu**Ph**), 7.23-7.21 (m, 6H, CH_2**Ph**), 7.17 (d, J=9.5 Hz, 4H, MeO**Ph**), 6.74 (d, J=9.2 Hz, 4H, MeO**Ph**), 6.65 (d, J=9.5 Hz, 4H, MeO**Ph**), 6.27 (s, 2H, triazole), 6.12-6.09 (m, 4H, CH_2**Ph**), 5.66 (d, J=4.3 Hz, 4H, β-pyrrole), 4.61 (s, 4H, **CH_2**Ph), 3.68 (s, 6H, OMe), 3.63 (s, 6H, OMe), 1.51 (s, 36H, ^{t}Bu), 1.45 (s, 36H, ^{t}Bu); ^{1}H NMR (600 MHz, [D_1]chloroform-[D5]pyridine (10:1 v/v), as **1-[D_5]pyridine**, Figure S1a): δ=9.20 (d, J=4.6 Hz, 2H, β-pyrrole), 8.89 (d, J=4.5 Hz, 2H, β-pyrrole), 8.79 (d, J=4.6 Hz, 2H, β-pyrrole), 8.74 (d, J=4.5 Hz, 2H, β-pyrrole), 8.16 (s, 1H, triazole), 7.90 (d, J=1.7 Hz, 4H, 3,5-di-^{t}Bu**Ph**), 7.67 (dd, J=1.7, 1.7 Hz, 2H, 3,5-di-^{t}Bu**Ph**), 7.47 (d, J=7.6 Hz, 2H, CH_2**Ph**), 7.39 (dd, J=7.6, 7.6 Hz, 2H, CH_2**Ph**), 7.32 (dd, J=7.4, 7.4 Hz, 1H, CH_2**Ph**), 7.12 (d, J=9.2 Hz, 4H, MeO**Ph**), 6.60 (d, J=9.4 Hz, 4H, MeO**Ph**), 5.84 (s, 2H, **CH_2**Ph), 3.58 (s, 6H, OMe), 1.41 (s, 36H, ^{t}Bu); ^{13}C NMR (150 MHz, [D_1]chloroform, as $\mathbf{1_2}$, Figure S1d): δ=153.07, 152.93, 152.43, 149.83, 149.51, 148.60, 148.00, 147.74, 147.35, 147.18, 145.66, 142.52, 133.76, 132.04, 130.10, 129.11, 128.49, 128.15, 128.02, 126.79, 126.15, 124.51, 123.98, 123.22, 123.04, 121.30, 120.77, 114.16, 114.13, 99.01, 55.57, 55.36, 53.14, 34.97, 34.90, 32.03, 31.74 (37 out of 38 inequivalent carbons are identified; the rest might have a small split of the chemical shift induced by the dimerization.); ^{13}C NMR (150 MHz, [D_1]chloroform-[D5]pyridine (10:1 v/v), as **1-[D_5]pyridine**, Figure S1c) δ=152.86, 152.03, 150.46, 150.17, 149.67, 149.24, 148.02, 146.97, 141.79, 132.76, 132.41, 130.35, 130.06, 129.52, 129.04, 128.56, 127.85, 126.68, 122.61, 121.88, 120.31, 114.04, 106.96, 55.14, 54.21, 34.71, 31.48 (27 out of 29 inequivalent carbons are identified; the rest are possibly concealed by the peaks derived from [D_5]pyridine.); HR-FAB-MS (as **1**): m/z 1132.5070; calcd for $C_{73}H_{85}N_5O_2SiZn$, [M^+]: 1132.5067.

Electrochemistry. $TBAPF_6$ as a supporting electrolyte was recrystallized from EtOH, dried at 120°C, and then put into vacuo for 24 h. A series of measurements was carried out under a Ar atmosphere in a standard one-component cell, using 3mmϕ glassy carbon (BAS) as a working electrode, platinum wire as a counter electrode, and an Ag/$AgNO_3$ reference electrode (0.01M $AgNO_3$ in 0.1M-TBAP/acetonitrile, BAS). As an internal standard, decamethylferrocene ($E^{0'}$ = -550 mV vs Fc^+/Fc in 0.1M TBAH-dichloromethane) was added after each measurement.

Fluorescence spectroscopy. All solutions were deoxygenized in quartz cells with N_2 bubbling.

Deconvolution of the UV/vis spectrum at $[\mathbf{1}]_{total}=5.9\times10^{-6}$ M. The deconvolution needs the spectra of dimer $\mathbf{1_2}$ and monomer **1**. As the spectrum of $\mathbf{1_2}$, that at $[\mathbf{1}]_{total}=1.0\times10^{-4}$ M is adopted: At this concentration the quantitative dimerization is observed in the ^{1}H NMR spectroscopy (Figure S2). The spectrum of **1** is estimated as follows: The differential spectrum between the spectra at $[\mathbf{1}]_{total}=1.2\times10^{-6}$ M and $[\mathbf{1}]_{total}=1.0\times10^{-4}$ M (Figure S3a) shows a peak at 24030 cm^{-1} (416.2 nm), which should correspond to the maximum of the B band of monomer **1** (Figure S3b). Then we move the spectrum of **1-py** (peak maximum: 23580 cm^{-1} (424.1 nm)) to the maximum of the differential spectrum with the intensity unchanged, and the resultant spectrum is regarded as that of **1** (Figure S3c). We note that the axial coordination of pyridine to ZnTPP results in a redshift of the B band (502 cm^{-1}) with a negligible change in its intensity.[4]

DFT calculation. The three-parameterized Becke-Lee-Yang-Parr (B3LYP) hybrid exchange-correlation functional was employed. As a basis set LanI2DZ was used for all atoms. The geometries were optimized with the C_i symmetry constraint. Solvent effects were not considered in the geometry optimization. This series of calculations was implemented with Gaussian 03 program.

Apparatus. Electrochemical data were recorded with a BAS ALS-620C voltammetric analyzer. UV/Vis/NIR spectra were measured with a Shimadzu UV-3150 spectrometer, NMR spectra with a Bruker DRX 600 (600 MHz) spectrometer, Fluorescence spectra with a Shimadzu RF-5300PC spectrofluorimeter, and PL quantum yields with a Hamamatsu Photonics C9920-02G absolute PL quantum yield measurement system.

References for Supporting Information

[1] C. Maeda, S. Yamaguchi, C. Ikeda, H. Shinokubo, A. Osuka, *Org. Lett.* **2008**, *10*, 549–552.

[2] C.-W. Lee, H.-P. Lu, C.-M. Lan, Y.-L. Huang, Y.-R. Liang, W.-N. Yen, Y.-C. Liu, Y.-S. Lin, E. W.-G. Diau, C.-Y. Yeh, *Chem. Eur. J.* **2009**, *15*, 1403–1412.

[3] H. Zhang, Q. Cai, D. Ma, *J. Org. Chem.* **2005**, *70*, 5164-5173.

[4] K. M. Kadish, L. R. Shiue, *Inorg. Chem.* **1982**, *21*, 3623-3630.

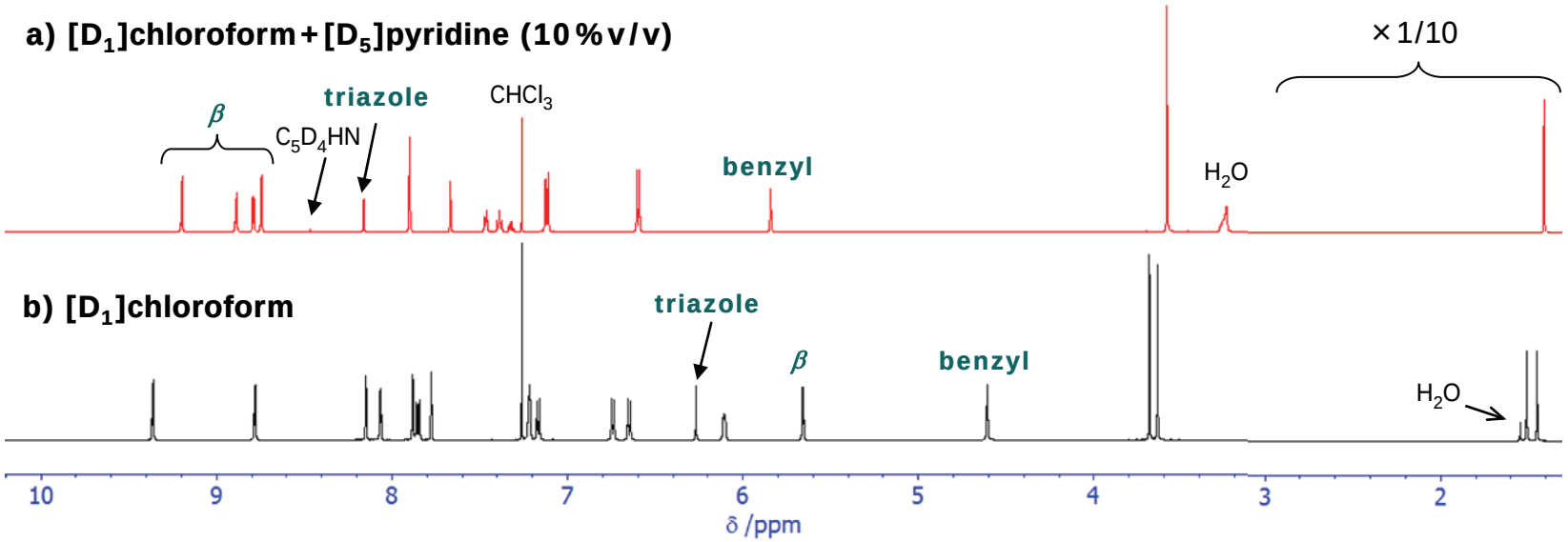

Figure S1 ^{1}H and ^{13}C NMR spectra in $[D_1]$chloroform: a) ^{1}H NMR, **1-[D$_5$]py** (5.0×10^{-3} M) with $[D_5]$pyridine (10%v/v); b) ^{1}H NMR, **1$_2$** ($[\mathbf{1}]_{total} = 5.0\times10^{-3}$ M).

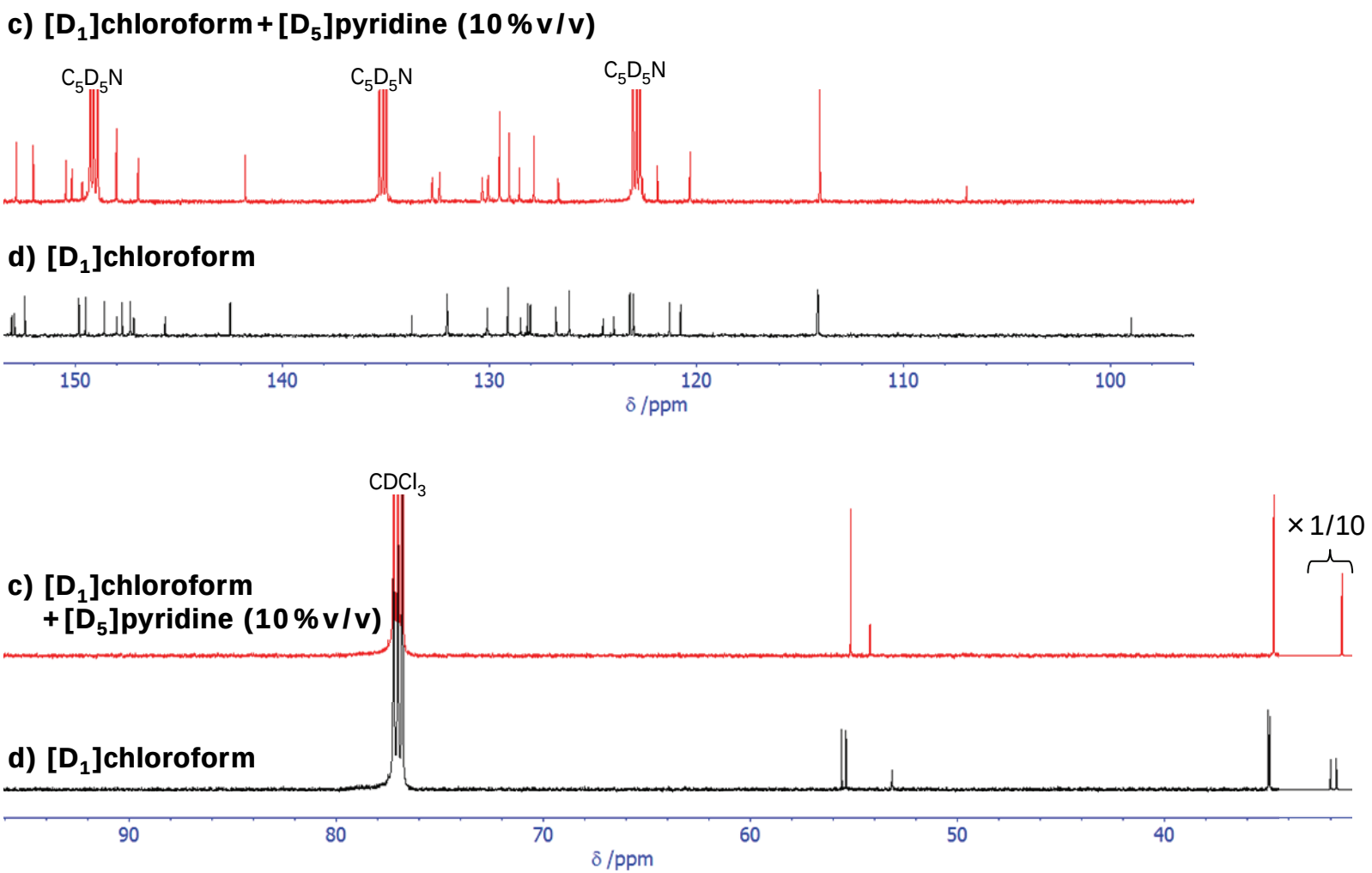

Figure S1 ^{1}H and ^{13}C NMR spectra in [D_1]chloroform: c) ^{13}C NMR, **1-[D_5]py** (5.0×10^{-3} M) with [D_5]pyridine (10%v/v); d) ^{13}C NMR, $\mathbf{1}_2$ ($[\mathbf{1}]_{total} = 5.0\times10^{-3}$ M) (Continued).

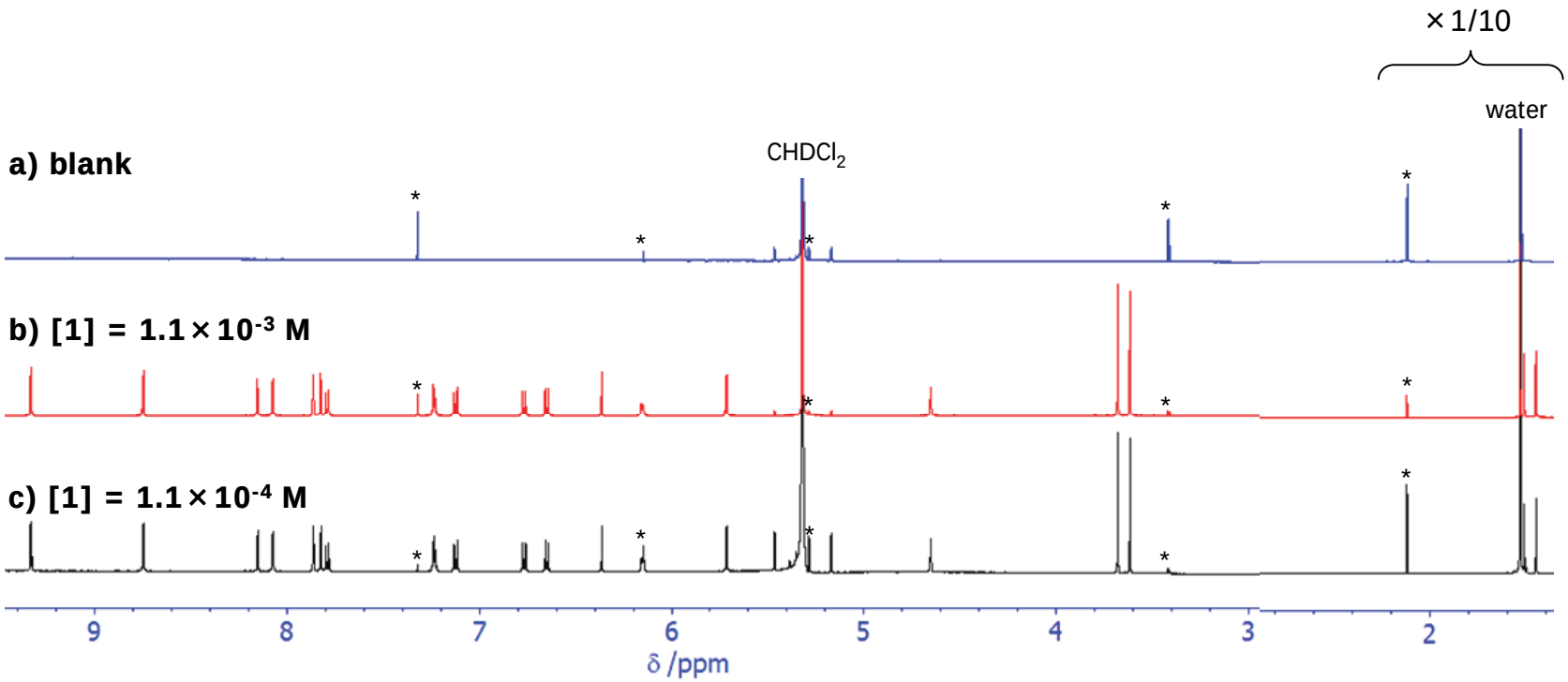

Figure S2 ^{1}H NMR spectra in [D_2]dichloromethane: a) blank; b) $\mathbf{1_2}$ ($[\mathbf{1}]_{total}$ = 1.1×10^{-3} M); c) $\mathbf{1_2}$ ($[\mathbf{1}]_{total}$ = 1.1×10^{-4} M). Asterisk indicates the signals of the impurities contaminated by the treatment of [D_2]dichloromethane with CaH_2 for the removal of acidic impurities. Neither emergence of a new signal nor shift of the existing signals upon a dilution indicates that $\mathbf{1_2}$ quantitatively sustains its dimeric form at these concentrations.

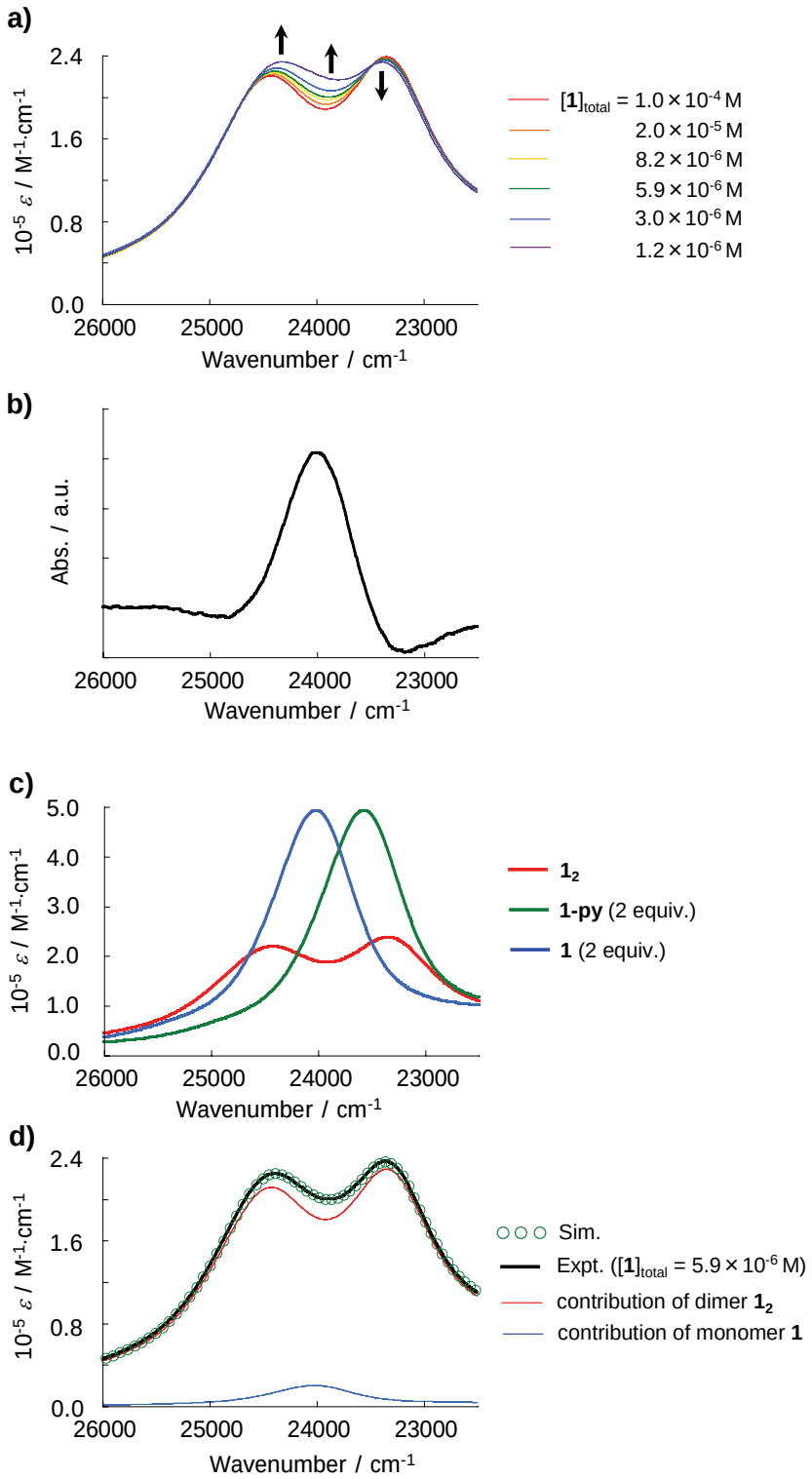

Figure S3 a) Concentration dependence of the UV/vis spectrum of **1** around the B band in dichloromethane. b) Differential spectrum between the spectra at $[\mathbf{1}]_{total}$ = 1.2×10^{-6} M and 1.0×10^{-4} M. c) Experimental (for $\mathbf{1_2}$ and **1-py**) and estimated (for **1**) spectra in dichloromethane. c) Deconvolution of the spectrum at $[\mathbf{1}]_{total}$ = 5.9×10^{-6} M. This deconvolution gives the ratio $[\mathbf{1_2}]/[\mathbf{1}]$ of 11.5, and association constant K_a of 4.7×10^{7} M^{-1}.

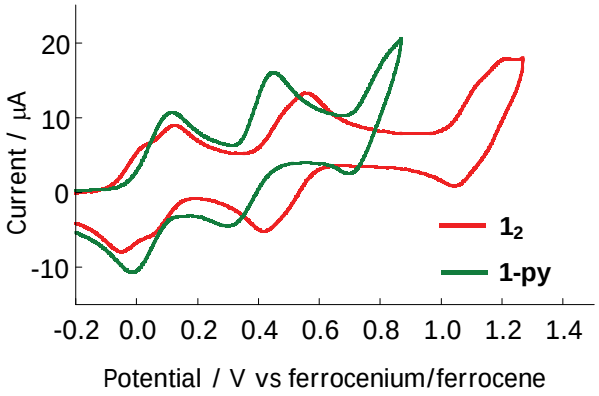

Figure S4 Cyclic voltammograms of **1_2** ($[\mathbf{1}]_{total}$ = 9.0×10^{-4} M) and **1-py** (9.0×10^{-4} M, with 150 equiv. of pyridine) in 0.1 M $TBAPF_6$-dichloromethane at a sweep rate of 100 mVs^{-1}.

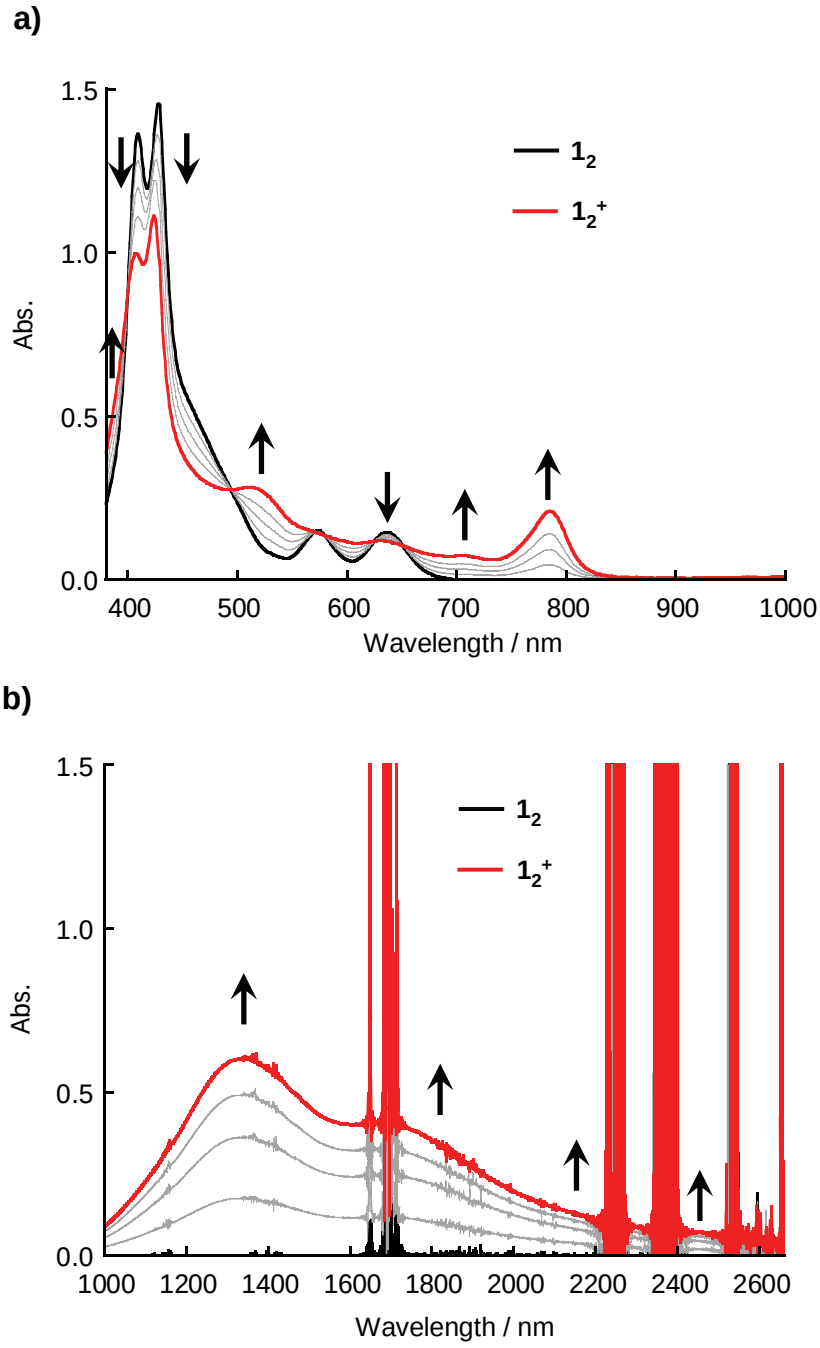

Figure S5 UV/vis/NIR spectral change of $\mathbf{1_2}$ in dichloromethane upon the oxidation to $\mathbf{1_2}^+$ by a titration with tris(4-bromophenyl)ammoniumyl hexachloroantimonate: a) $[\mathbf{1}]_{total} = 1.2\times10^{-5}$ M; b) $[\mathbf{1}]_{total} = 9.8\times10^{-5}$ M. The dilution factors are corrected.

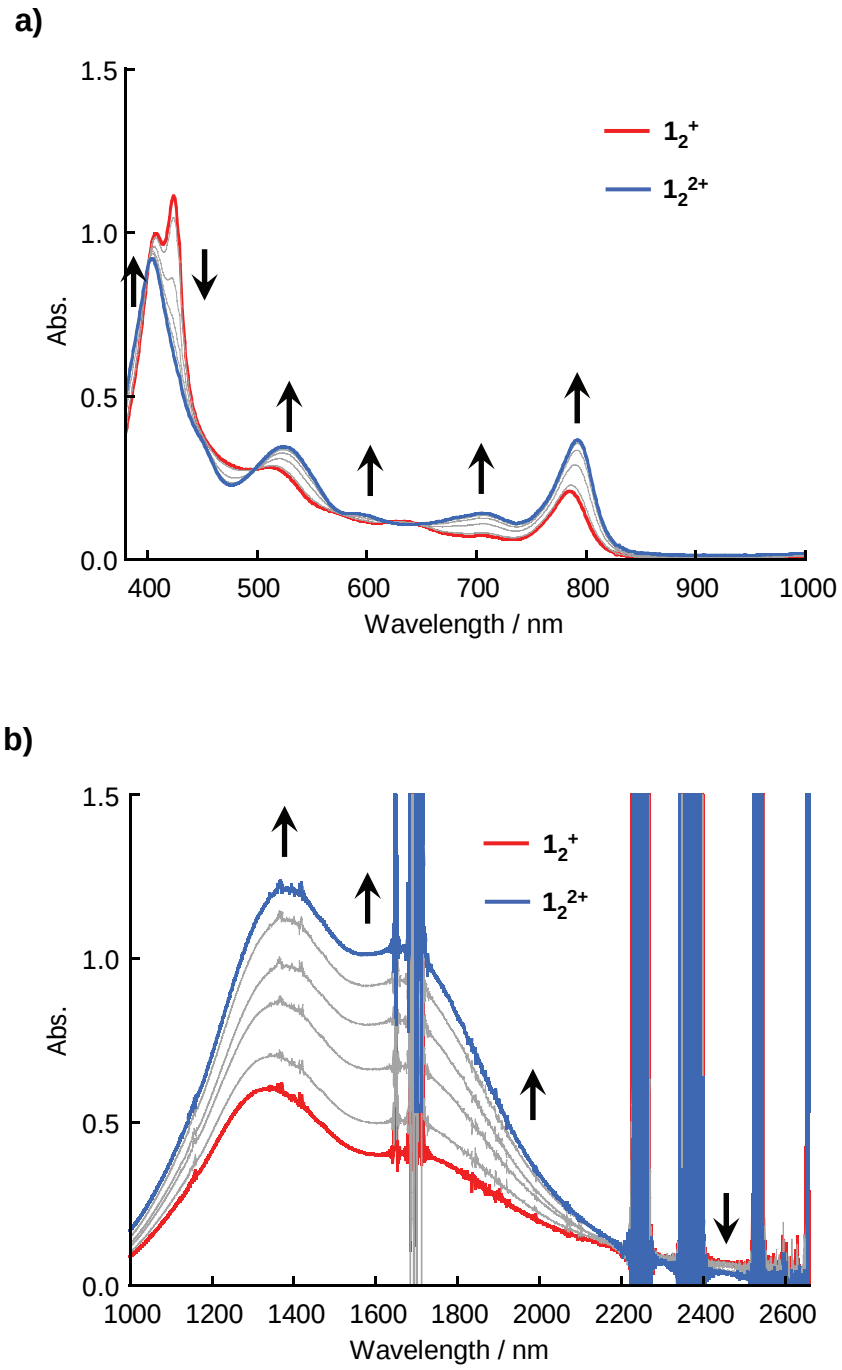

Figure S6 UV/vis/NIR spectral change of $\mathbf{1}_2^+$ in dichloromethane upon the oxidation to $\mathbf{1}_2^{2+}$ by a titration with tris(4-bromophenyl)ammoniumyl hexachloroantimonate: a) $[\mathbf{1}]_{total}$ = 1.2×10^{-5} M; b) $[\mathbf{1}]_{total}$ = 9.8×10^{-5} M. The dilution factors are corrected.

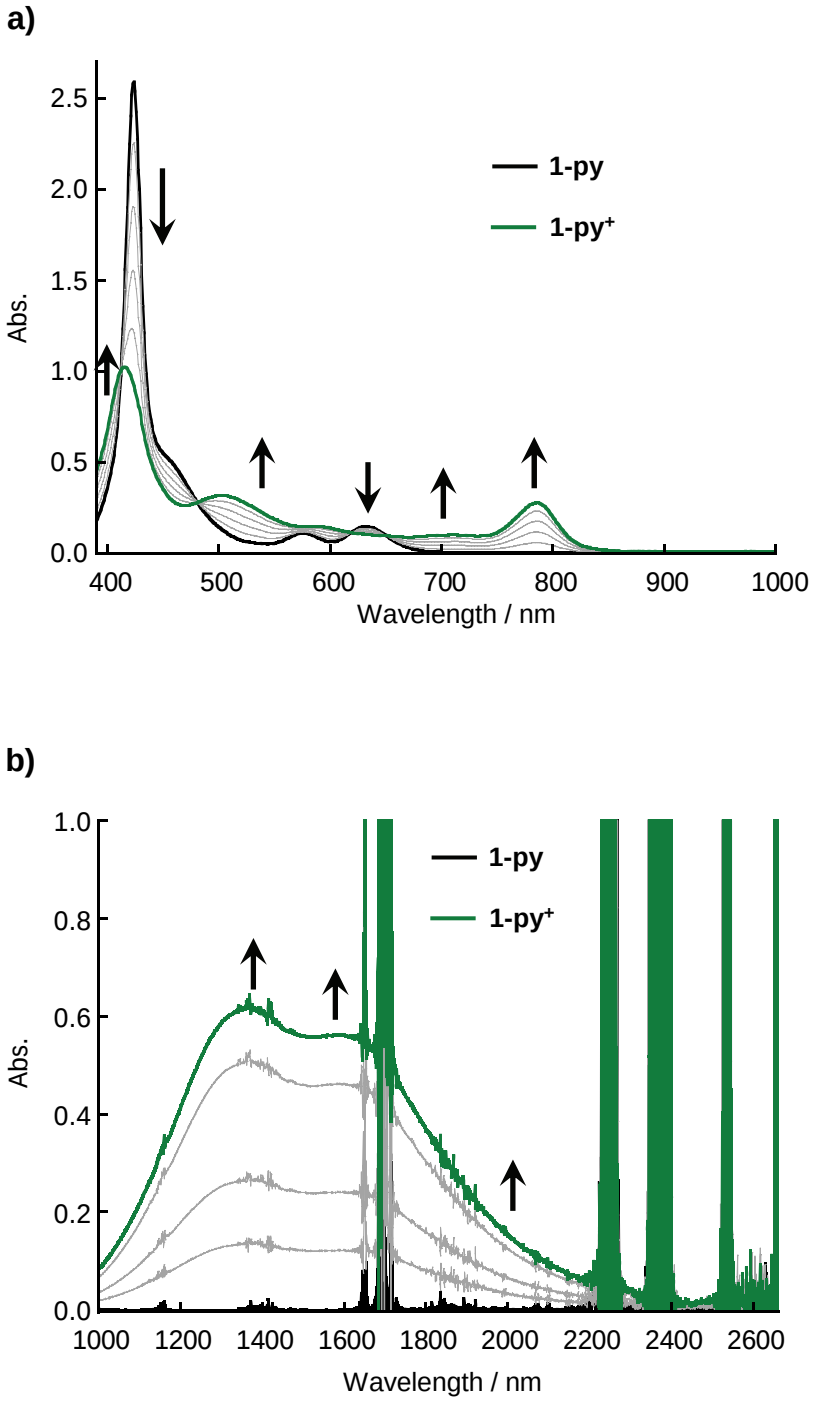

Figure S7 UV/vis/NIR spectral change of **1-py** in dichloromethane upon the oxidation to **1-py$^+$** by a titration with tris(4-bromophenyl)ammoniumyl hexachloroantimonate: a) 9.4×10^{-6} M; b) 5.6×10^{-5} M. The dilution factors are corrected.

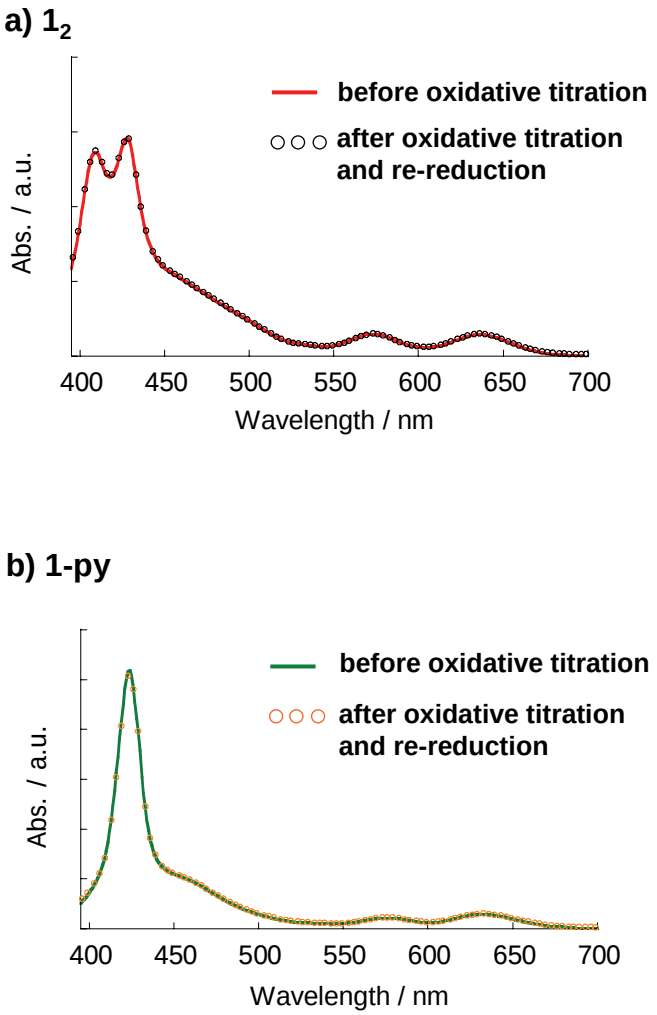

Figure S8 UV/Vis spectra in dichloromethane before the oxidative titration experiments shown in Figures S5-7, and upon re-reduction after the titration experiments: a) $\mathbf{1_2}$ ($[\mathbf{1}]_{total}=1.2\times10^{-5}$ M; b) **1-py** (9.4×10^{-6} M). Re-reduction was conducted with excess decamethylferrocene. The dilution factors are corrected. We note that the "re-reduction" spectra contain contributions from tris(4-bromophenyl)amine, decamethylferrocene, and decamethylferrocenium hexachloroantimonate, all of which have negligible absorptivities in the shown region.

Table S1 Parameters for the deconvolution of the NIR spectra shown in Figure 5: a) **1-py$^+$**; b) **1$_2^{2+}$**; c) **1$_2^+$**. Red ones in c) indicate the IVCT band.

a) 1-py$^+$

	$10^{-4}\varepsilon_{max}$ / $M^{-1}cm^{-1}$	$\bar{\nu}_{max}$ / cm^{-1}	σ / cm^{-1}
#1	0.082	10030	550
#2	0.197	9155	550
#3	0.487	8280	550
#4	0.804	7405	550
#5	0.935	6100	700

b) 1$_2^{2+}$

	$10^{-4}\varepsilon_{max}$ / $M^{-1}cm^{-1}$	$\bar{\nu}_{max}$ / cm^{-1}	σ / cm^{-1}
#1	0.255	9860	550
#2	0.467	8985	550
#3	1.030	8110	550
#4	1.918	7235	550
#5	1.916	5913	665

c) 1$_2^+$

	$10^{-4}\varepsilon_{max}$ / $M^{-1}cm^{-1}$	$\bar{\nu}_{max}$ / cm^{-1}	σ / cm^{-1}
#1	0.121	9925	550
#2	0.261	9050	550
#3	0.596	8175	550
#4	0.951	7300	550
#5	0.673	5920	665
#6	0.149	4600	1384

$$[Gaussian](\bar{\nu}) = \varepsilon_{max} \exp[-\frac{(\bar{\nu}-\bar{\nu}_{max})^2}{2\sigma^2}]$$

For IVCT band

$$\bar{\nu}_{1/2} = 2(2\ln 2)^{1/2}\sigma = (2310\bar{\nu}_{max})$$

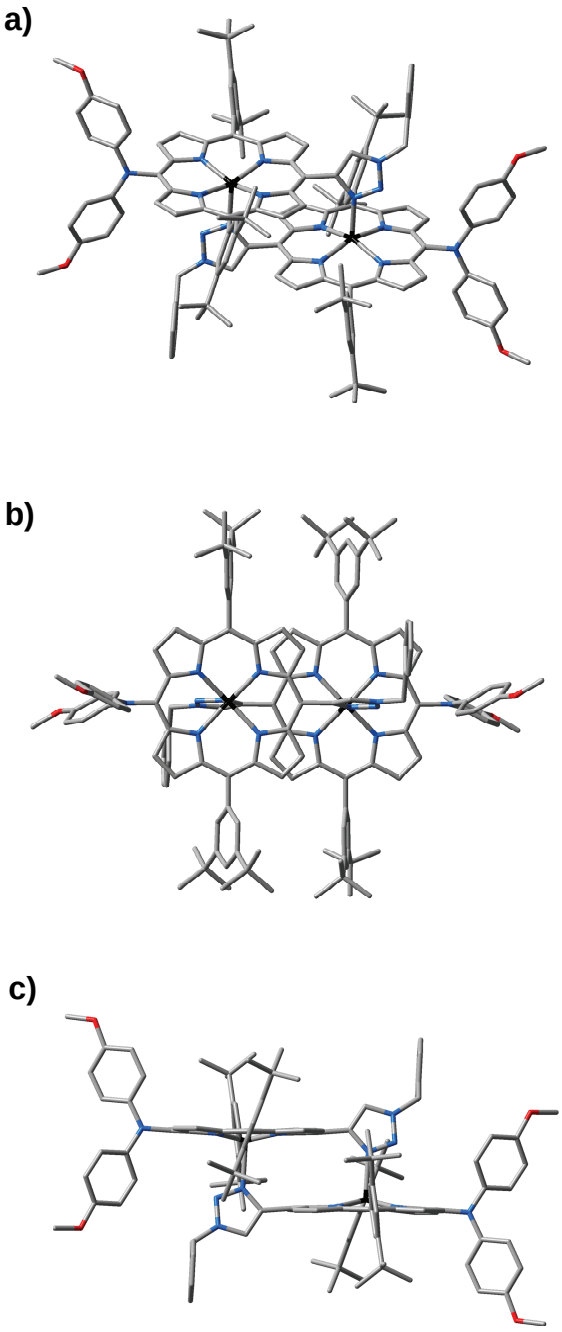

Figure S9 Optimized structure of $\mathbf{1}_2$ by a DFT calculation: a) oblique view; b) top view; c) side view. Gray, blue, red, and black indicates carbon, nitrogen, oxygen, and zinc atoms, respectively. Hydrogen atoms are omitted for clarity.

Table S2 Atomic coodinates of **1_2** optimized by the DFT calculation. Blue and red ones are those for the N atoms of the di-*p*-anisylamino groups and zinc atoms, respectively.

Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.71402	1.71878	1.39763
2	6	-0.71402	1.71878	2.85936
3	1	0.16631	1.71878	3.48609
4	6	-2.84980	1.68880	2.05902
5	6	-4.26303	1.70383	2.05255
6	6	-5.06829	1.77266	0.89016
7	6	-6.52900	1.82603	0.89058
8	1	-7.14960	1.80356	1.77466
9	6	-6.93313	1.91394	-0.42070
10	1	-7.94111	1.98386	-0.80253
11	6	-5.72501	1.91706	-1.23807
12	6	-5.70809	2.01833	-2.64707
13	6	-4.55417	2.04056	-3.46323
14	6	-4.56683	2.26950	-4.90273
15	1	-5.45569	2.41037	-5.50022
16	6	-3.25524	2.29423	-5.31611
17	1	-2.88244	2.46986	-6.31440
18	6	-2.42299	2.08004	-4.13209
19	6	-1.00384	2.10533	-4.12334
20	6	-0.19917	2.00702	-2.96253
21	6	1.26095	2.06620	-2.95238
22	1	1.88333	2.15695	-3.83021
23	6	1.66499	1.96695	-1.64388
24	1	2.67733	1.96151	-1.26616
25	6	0.45925	1.83745	-0.83036
26	6	0.44364	1.76610	0.58359
27	6	-4.97146	1.67254	3.38223
28	6	-5.20758	0.44048	4.03185
29	1	-4.85750	-0.46664	3.55137
30	6	-5.88625	0.38501	5.26362
31	6	-6.31629	1.60633	5.84012
32	1	-6.83777	1.57560	6.79081
33	6	-6.09526	2.85244	5.22345
34	6	-5.41742	2.86233	3.97990
35	1	-5.22976	3.80075	3.46412
36	6	-0.31406	2.30607	-5.44573
37	6	-0.34699	1.29610	-6.42917
38	1	-0.85709	0.36853	-6.19344
39	6	0.27063	1.47466	-7.68487
40	6	0.92295	2.70338	-7.92913
41	1	1.40241	2.85787	-8.89279
42	6	0.97533	3.74018	-6.97093
43	6	0.34939	3.51863	-5.72620
44	1	0.35387	4.28930	-4.96325
45	6	1.75624	1.84101	1.27731
46	6	0.71402	-1.71878	-1.39763
47	6	0.71402	-1.71878	-2.85936
48	1	-0.16631	-1.71878	-3.48609
49	6	2.02646	-1.70296	-3.26427
50	1	2.40884	-1.70009	-4.27468
51	6	2.84980	-1.68880	-2.05902
52	6	4.26303	-1.70383	-2.05255
53	6	5.06829	-1.77266	-0.89016
54	6	6.52900	-1.82603	-0.89058
55	1	7.14960	-1.80356	-1.77466
56	6	6.93313	-1.91394	0.42070
57	1	7.94111	-1.98386	0.80253
58	6	5.72501	-1.91706	1.23807
59	6	5.70809	-2.01833	2.64707
60	6	4.55417	-2.04056	3.46323
61	6	4.56683	-2.26950	4.90273
62	1	5.45569	-2.41037	5.50022
63	6	3.25524	-2.29423	5.31611
64	1	2.88244	-2.46986	6.31440
65	6	2.42299	-2.08004	4.13209
66	6	1.00384	-2.10533	4.12334
67	6	0.19917	-2.00702	2.96253
68	6	-1.26095	-2.06620	2.95238
69	1	-1.88333	-2.15695	3.83021
70	6	-1.66499	-1.96695	1.64388
71	1	-2.67733	-1.96151	1.26616
72	6	-0.45925	-1.83745	0.83036
73	6	-0.44364	-1.76610	-0.58359
74	6	4.97146	-1.67254	-3.38223
75	6	5.20758	-0.44048	-4.03185
76	1	4.85750	0.46664	-3.55137
77	6	5.88625	-0.38501	-5.26362
78	6	6.31629	-1.60633	-5.84012
79	1	6.83777	-1.57560	-6.79081
80	6	6.09526	-2.85244	-5.22345
81	6	5.41742	-2.86233	-3.97990
82	1	5.22976	-3.80075	-3.46412
83	6	0.31406	-2.30607	5.44573
84	6	0.34699	-1.29610	6.42917
85	1	0.85709	-0.36853	6.19344
86	6	-0.27063	-1.47466	7.68487
87	6	-0.92295	-2.70338	7.92913
88	1	-1.40241	-2.85787	8.89279
89	6	-0.97533	-3.74018	6.97093
90	6	-0.34939	-3.51863	5.72620
91	1	-0.35387	-4.28930	4.96325
92	6	-1.75624	-1.84101	-1.27731
93	6	-2.02646	1.70296	3.26427
94	1	-2.40884	1.70009	4.27468
95	7	-2.02276	1.68965	0.93839
96	7	-4.60752	1.81774	-0.42080
97	7	-3.24370	1.91963	-3.02158
98	7	-0.65695	1.85096	-1.65573
99	7	2.68386	0.80367	1.36255
100	7	2.02276	-1.68965	-0.93839
101	7	4.60752	-1.81774	0.42080
102	7	3.24370	-1.91963	3.02158
103	7	0.65695	-1.85096	1.65573
104	7	-2.68386	-0.80367	-1.36255
105	**30**	**-2.63302**	**1.45234**	**-1.05724**
106	**30**	**2.63302**	**-1.45234**	**1.05724**
107	**7**	**6.98875**	**-2.16019**	**3.31446**
108	**7**	**-6.98875**	**2.16019**	**-3.31446**
109	6	7.64599	-3.43205	3.28193
110	6	9.05444	-3.53725	3.25508
111	6	6.88528	-4.62807	3.23875
112	6	9.69129	-4.79093	3.20674
113	1	9.66238	-2.63766	3.26672
114	6	7.51355	-5.87645	3.17360
115	1	5.80146	-4.57623	3.25125
116	6	8.91961	-5.96884	3.16396
117	1	6.93141	-6.79243	3.13668
118	6	-7.64599	3.43205	-3.28193
119	6	-9.05444	3.53725	-3.25508
120	6	-6.88528	4.62807	-3.23875

Table S2 Atomic coodinates of **1_2** optimized by the DFT calculation (Continued).

Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
121	6	-9.69129	4.79093	-3.20674
122	1	-9.66238	2.63766	-3.26672
123	6	-7.51355	5.87645	-3.17360
124	1	-5.80146	4.57623	-3.25125
125	6	-8.91961	5.96884	-3.16396
126	1	-6.93141	6.79243	-3.13668
127	6	7.56130	-1.01779	3.95574
128	6	7.36471	0.27815	3.41499
129	6	8.31751	-1.13781	5.14293
130	6	7.91886	1.40373	4.03643
131	1	6.77979	0.39354	2.50809
132	6	8.88346	-0.01062	5.76560
133	1	8.46818	-2.11798	5.58549
134	6	8.68605	1.26932	5.21065
135	1	7.79324	2.39757	3.61501
136	1	9.46020	-0.14591	6.67561
137	6	-7.56130	1.01779	-3.95574
138	6	-7.36471	-0.27815	-3.41499
139	6	-8.31751	1.13781	-5.14293
140	6	-7.91886	-1.40373	-4.03643
141	1	-6.77979	-0.39354	-2.50809
142	6	-8.88346	0.01062	-5.76560
143	1	-8.46818	2.11798	-5.58549
144	6	-8.68605	-1.26932	-5.21065
145	1	-7.79324	-2.39757	-3.61501
146	1	-9.46020	0.14591	-6.67561
147	8	9.20372	2.46028	5.74028
148	8	-9.20372	-2.46028	-5.74028
149	6	9.98769	2.38640	6.96261
150	1	10.28052	3.41531	7.18256
151	1	9.39248	1.98622	7.79597
152	1	10.88681	1.76863	6.82472
153	6	-9.98769	-2.38640	-6.96261
154	1	-9.39248	-1.98622	-7.79597
155	1	-10.28052	-3.41531	-7.18256
156	1	-10.88681	-1.76863	-6.82472
157	1	10.77638	-4.82843	3.18843
158	1	-10.77638	4.82843	-3.18843
159	8	9.44582	-7.26814	3.10993
160	8	-9.44582	7.26814	-3.10993
161	6	10.89025	-7.42443	3.07298
162	1	11.06488	-8.50177	3.03072
163	1	11.32264	-6.94580	2.18240
164	1	11.36167	-7.01017	3.97616
165	6	-10.89025	7.42443	-3.07298
166	1	-11.32264	6.94580	-2.18240
167	1	-11.06488	8.50177	-3.03072
168	1	-11.36167	7.01017	-3.97616
169	7	-3.77001	-1.21446	-2.04261
170	7	-3.52749	-2.52140	-2.40439
171	6	-2.30335	-2.93374	-1.94985
172	6	2.30335	2.93374	1.94985
173	7	3.77001	1.21446	2.04261
174	7	3.52749	2.52140	2.40439
175	1	1.90587	3.91835	2.12709
176	1	-1.90587	-3.91835	-2.12709
177	6	4.54561	3.26218	3.17952
178	1	5.32168	2.52567	3.40804
179	1	4.98083	4.03567	2.53587
180	6	-4.54561	-3.26218	-3.17952
181	1	-4.98083	-4.03567	-2.53587
182	1	-5.32168	-2.52567	-3.40804
183	6	3.98039	3.88279	4.44791
184	6	3.44051	3.06212	5.46282
185	6	4.00953	5.27934	4.63218
186	6	2.93053	3.63441	6.64020
187	1	3.42564	1.98170	5.33152
188	6	3.50373	5.85427	5.81467
189	1	4.42867	5.91891	3.85712
190	6	2.96115	5.03252	6.81922
191	1	2.51683	2.99682	7.41697
192	1	3.53197	6.93287	5.94823
193	1	2.56754	5.47385	7.73167
194	6	-3.98039	-3.88279	-4.44791
195	6	-3.44051	-3.06212	-5.46282
196	6	-4.00953	-5.27934	-4.63218
197	6	-2.93053	-3.63441	-6.64020
198	1	-3.42564	-1.98170	-5.33152
199	6	-3.50373	-5.85427	-5.81467
200	1	-4.42867	-5.91891	-3.85712
201	6	-2.96115	-5.03252	-6.81922
202	1	-2.51683	-2.99682	-7.41697
203	1	-3.53197	-6.93287	-5.94823
204	1	-2.56754	-5.47385	-7.73167
205	6	6.56596	-4.18954	-5.84398
206	6	7.56429	-4.88564	-4.87193
207	6	5.33625	-5.11873	-6.06782
208	6	7.27671	-3.99720	-7.20708
209	1	8.45277	-4.26074	-4.71216
210	1	7.10982	-5.07803	-3.89309
211	1	7.89169	-5.84888	-5.28692
212	1	4.62104	-4.65883	-6.76252
213	1	5.65820	-6.07991	-6.49197
214	1	4.80729	-5.32513	-5.13015
215	1	7.58400	-4.97448	-7.60142
216	1	6.61540	-3.53204	-7.94996
217	1	8.17873	-3.37871	-7.11188
218	6	-6.56596	4.18954	5.84398
219	6	-5.33625	5.11873	6.06782
220	6	-7.56429	4.88564	4.87193
221	6	-7.27671	3.99720	7.20708
222	1	-4.62104	4.65883	6.76252
223	1	-4.80729	5.32513	5.13015
224	1	-5.65820	6.07991	6.49197
225	1	-8.45277	4.26074	4.71216
226	1	-7.89169	5.84888	5.28692
227	1	-7.10982	5.07803	3.89309
228	1	-7.58400	4.97448	7.60142
229	1	-8.17873	3.37871	7.11188
230	1	-6.61540	3.53204	7.94996
231	6	6.17988	0.94786	-5.99348
232	6	5.50159	0.93507	-7.39504
233	6	5.65106	2.17781	-5.21413
234	6	7.71874	1.11449	-6.16934
235	1	5.85673	0.09933	-8.01020
236	1	4.41204	0.84519	-7.29925
237	1	5.72239	1.86761	-7.93296
238	1	6.11682	2.26256	-4.22374
239	1	5.88437	3.09385	-5.77248
240	1	4.56216	2.13665	-5.08043

Table S2 Atomic coodinates of **1_2** optimized by the DFT calculation (Continued).

Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
241	1	7.94292	2.05749	-6.68673
242	1	8.22324	1.12934	-5.19447
243	1	8.15170	0.29712	-6.75865
244	6	-6.17988	-0.94786	5.99348
245	6	-5.65106	-2.17781	5.21413
246	6	-5.50159	-0.93507	7.39504
247	6	-7.71874	-1.11449	6.16934
248	1	-6.11682	-2.26256	4.22374
249	1	-4.56216	-2.13665	5.08043
250	1	-5.88437	-3.09385	5.77248
251	1	-5.85673	-0.09933	8.01020
252	1	-5.72239	-1.86761	7.93296
253	1	-4.41204	-0.84519	7.29925
254	1	-7.94292	-2.05749	6.68673
255	1	-8.15170	-0.29712	6.75865
256	1	-8.22324	-1.12934	5.19447
257	6	1.69383	5.06757	-7.31550
258	6	1.66166	6.08022	-6.14339
259	6	3.18439	4.77933	-7.66193
260	6	1.00016	5.72804	-8.54370
261	1	0.63501	6.35704	-5.87170
262	1	2.15858	5.68331	-5.24864
263	1	2.18682	6.99856	-6.43691
264	1	3.27975	4.09285	-8.51199
265	1	3.70044	5.71315	-7.92436
266	1	3.70289	4.32822	-6.80614
267	1	1.50365	6.66922	-8.80397
268	1	1.02842	5.07635	-9.42538
269	1	-0.05196	5.95054	-8.32377
270	6	-1.69383	-5.06757	7.31550
271	6	-3.18439	-4.77933	7.66193
272	6	-1.66166	-6.08022	6.14339
273	6	-1.00016	-5.72804	8.54370
274	1	-3.27975	-4.09285	8.51199
275	1	-3.70289	-4.32822	6.80614
276	1	-3.70044	-5.71315	7.92436
277	1	-0.63501	-6.35704	5.87170
278	1	-2.18682	-6.99856	6.43691
279	1	-2.15858	-5.68331	5.24864
280	1	-1.50365	-6.66922	8.80397
281	1	0.05196	-5.95054	8.32377
282	1	-1.02842	-5.07635	9.42538
283	6	0.25207	0.38555	-8.78499
284	6	-0.52075	-0.88420	-8.34717
285	6	-0.43563	0.94890	-10.06374
286	6	1.71189	-0.03263	-9.12918
287	1	-0.06518	-1.35572	-7.46680
288	1	-1.56965	-0.65631	-8.11470
289	1	-0.50897	-1.61890	-9.16314
290	1	0.08668	1.83216	-10.45028
291	1	-0.44409	0.18921	-10.85750
292	1	-1.47347	1.23824	-9.85336
293	1	1.71268	-0.79742	-9.91812
294	1	2.30414	0.81878	-9.48566
295	1	2.21724	-0.44767	-8.24762
296	6	-0.25207	-0.38555	8.78499
297	6	0.43563	-0.94890	10.06374
298	6	0.52075	0.88420	8.34717
299	6	-1.71189	0.03263	9.12918
300	1	-0.08668	-1.83216	10.45028
301	1	1.47347	-1.23824	9.85336
302	1	0.44409	-0.18921	10.85750
303	1	0.06518	1.35572	7.46680
304	1	0.50897	1.61890	9.16314
305	1	1.56965	0.65631	8.11470
306	1	-1.71268	0.79742	9.91812
307	1	-2.21724	0.44767	8.24762
308	1	-2.30414	-0.81878	9.48566