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Supporting Information

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Highly Fluorescent Self-Coordinated Phthalocyanine Dimers

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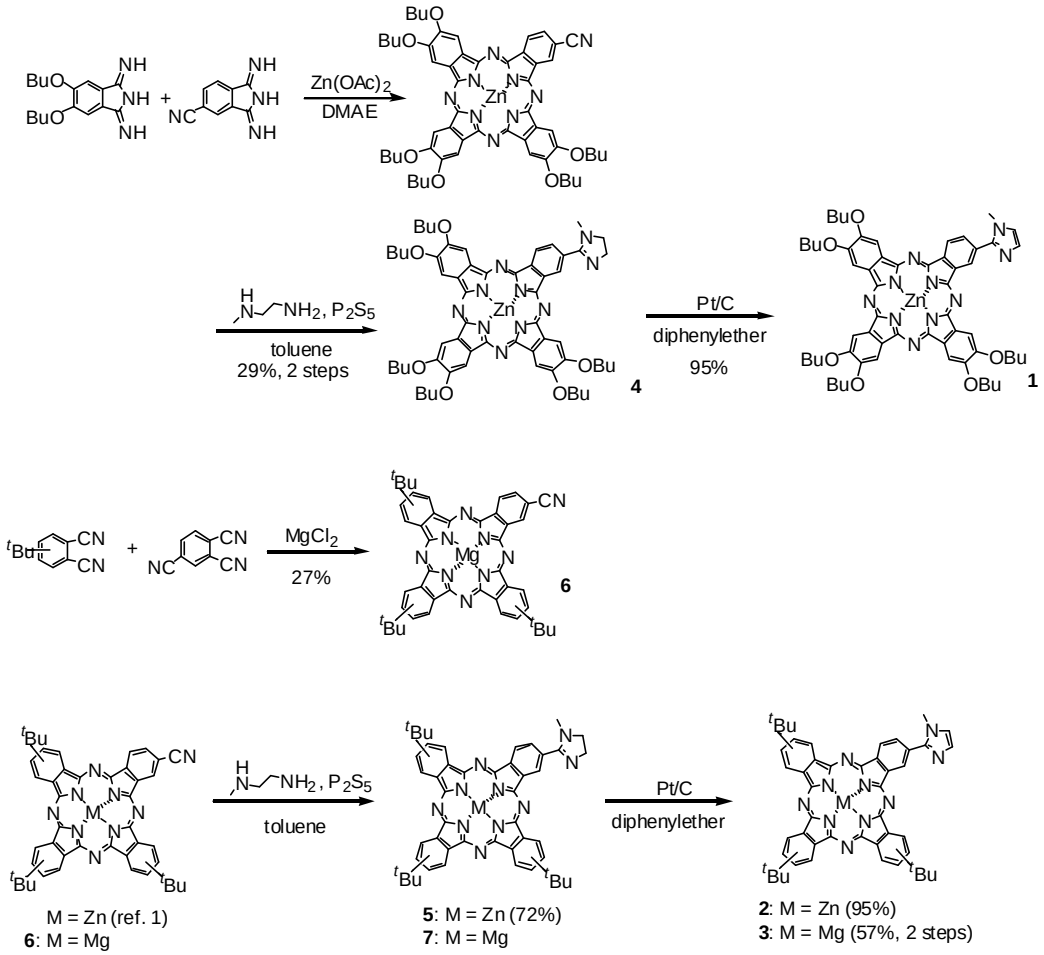
General procedure

^{1}H NMR, ^{1}H-^{13}C HMQC, ^{1}H-^{1}H TOCSY and ^{1}H-^{13}C HMBC spectra were recorded on JEOL ECP-600 (600 MHz NMR) spectrometer using TMS (0 ppm) as an internal standard. MALDI-TOF mass spectra were measured by Perseptive Biosystems Voyager DE-STR with dithranol (Aldrich) as a matrix. UV-vis absorption spectra were obtained with a Shimadzu UV-3100PC spectrometer. Fluorescence spectra were obtained by using a Hitachi F-4500 spectrometer. Column chromatography was performed with silica gel (63-210 μm, KANTO Chemical Co., Inc.). All chemicals obtained from commercial sources were used without further purification, unless otherwise noted.

Electrochemical Measurements

The experimental system for differential pulse voltammetry (DPV) employed CH_2Cl_2 (distilled over CaH_2), in the presence of 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($^{n}Bu_4N{\cdot}PF_6$) as supporting electrolyte (recrystallized from ethanol and dried at 45 °C in vacuo prior to use). A platinum pad (diameter 1.6 mm), a platinum wire, and Ag/AgCl (sat. KCl) were used as a working (WE), a counter (CE), and a reference electrode, respectively. The experimental set-up employed the conventional three-electrodes system consisting of two compartments. A sample solution was



Scheme S1. Synthetic pathways of **1, 2** and **3**.

put into the tube equipped with a Vycol glass junction inside the organic compartment of 0.1 M $^{n}Bu_4N{\cdot}PF_6$ solution. Another compartment contained sat. KCl aq. These organic and aqueous compartments were connected via an agar salt bridge. The CE and WE were set in the sample solution and the RE was put into the aqueous compartment. The voltammograms were recorded on a potentiostat (BAS CV-50W).

Procedures of Synthesis

Hexa-*n*-butoxyimidazolynylphthalocyaninatozinc (4)

6-Cyano-1,3-diiminoisoindoline[1] (60 mg, 0.35 mmol) and 6,7-dibutoxydiiminoisoindoline[2] (500 mg, 1.75 mmol) were dissolved in dimethylaminoethanol (DMAE, 70.0 mL). The mixture was refluxed under N_2 for 12 h in the presence of zinc acetate (271 mg, 1.24 mmol). After the mixture was concentrated under reduced pressure, the solid residue was washed with water and methanol. The crude products were dissolved in dry toluene (3.0 mL). The solution was added to *N*-methylethylenediamine (850 mg, 11.5 mmol, freshly distilled over KOH) and 4.0 mg of P_2S_5, and then the mixture was heated at 95 °C for 6 h. The reaction mixture was then cooled, poured into cold water and extracted with benzene. The organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, $CHCl_3$/pyridine = 60:1 followed by $CHCl_3$/pyridine/Et_3N = 60:2:1) to afford **4** (112 mg, 29% yield based on 6-cyano-1,3-diiminoisoindoline) as a blue solid.

From ^{1}H NMR measurements, two kinds of isomeric dimers were observed for complementary dimer of **4**. The ratio of the isomers was estimated as 2:1 from the integration areas of well-separated peaks (7.28 and 6.90, and 1.72 and 1.56). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) *d* 9.20-9.12 (m, 1 H, Ar-H), 9.11-8.92 (m, 6 H, Ar-H), 7.28 (s, 0.34 H, Ar-H), 6.90 (s, 0.66 H, Ar-H), 5.47-5.43 (m, 1 H, Ar-H), 5.06-4.40 (m, 12 H, -O-$\underline{CH_2}$-CH_2-CH_2-CH_3), 2.31-2.14 (m, 14H, -O-CH_2-$\underline{CH_2}$-CH_2-CH_3, Im-H), 1.94-1.77 (m, 12H, -O-CH_2-CH_2-$\underline{CH_2}$-CH_3), 1.72 (s, 1 H, *N*-$\underline{Me}$), 1.56 (s, 2 H, *N*-$\underline{Me}$), 1.32-1.17 (m, 18 H, -O-CH_2-CH_2-CH_2-$\underline{CH_3}$), 0.24-(-0.06) (m, 2 H, Im-H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) *d* 153.81, 151.71, 139.04, 137.60, 132.72, 124.20, 122.69, 119.20, 106.18, 69.72, 49.53, 46.69, 32.66, 31.77, 19.62, 14.20; MALDI-TOF MS: *m/z* calcd for

$C_{120}H_{140}N_{20}O_{12}Zn_2$ [dimer] 2180.95, $C_{60}H_{70}N_{10}O_6Zn$ [monomer] 1090.48, found 2181.98 [dimer, $(M+H)^+$], 1091.57 [monomer, $(M+H)^+$]; UV-vis (toluene) [λ_{max} nm (logε)] 366 (4.90), 613 (4.50), 670 (5.08), 699 (5.21).

Hexa-*n*-butoxyimidazolylphthalocyaninatozinc (1)

A mixture of **4** (20 mg, 0.018 mmol) and activated 5% Pt/C (1.0 mg) were refluxed for 5 h in diphenylether (10 mL). After removal of Pt/C catalyst, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, pyridine/$CHCl_3$ = 1:100) to afford **1** (19 mg, 95%) as a blue solid. From ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) measurements, two kinds of isomeric dimers [oblique (o) and parallel (p)] were obtained in a 1:1 ratio. **[1]$_2$**: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) *d* 9.27-8.82 (m, 7H, Ar-H, o and p), 7.44 (s, 0.5 H, Ar-H, p), 6.96 (s, 0.5 H, Ar-H, o), 5.57-5.47 (m, 2H, Ar-H and Im-H, o and p), 5.03-4.35 (m, 12 H, -O-$\underline{CH_2}$-CH_2-CH_2-CH_3, o and p), 2.91 (s, 0.5 H, Im-H, o), 2.83 (s, 0.5 H, Im-H, p), 2.55 (s, 1.5 H, *N*-$\underline{CH_3}$, o), 2.39 (s, 1.5 H, *N*-$\underline{CH_3}$, p), 2.29-2.11 (m, 12 H, -O-CH_2-$\underline{CH_2}$-CH_2-CH_3, o and p), 1.94-1.67 (m, 12H, -O-CH_2-CH_2-$\underline{CH_2}$-CH_3, o and p), 1.30-1.14 (m, 18H, -O-CH_2-CH_2-CH_2-$\underline{CH_3}$, o and p); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) *d* 153.08, 151.86 (Ar-C, o and p), 151.51, 149.94, 149.16, 144.22 (Im-C, p), 143.98 (Im-C, o), 139.31 (Ar-C, o and p), 135.04, 131.12, 130.34, 124.85 (Ar-C, o and p), 121.71 (Ar-C, p), 120.48 (Im-C, p), 120.26 (Im-C, o), 120.14 (Ar-C, o), 118.57 (Im-C, o), 117.00 (Im-C, p), 106.02 (Ar-C, o and p), 104.46 (Ar-C, o and p), 102.89 (Ar-C, o and p), 68.38 (-O-$\underline{CH_2}$-CH_2-CH_2-CH_3, o and p), 31.50 (*N*-CH_3, o), 30.73 (*N*-CH_3, p), 29.83

(-O-CH_2-$\underline{CH_2}$-CH_2-CH_3, o and p), 18.18 (-O-CH_2-CH_2-$\underline{CH_2}$-CH_3, o and p), 11.91 (-O-CH_2-CH_2-CH_2-$\underline{CH_3}$, o and p); MALDI-TOF MS: *m/z* calcd for $C_{120}H_{136}N_{20}O_{12}Zn_2$ (dimer) 2176.92, $C_{60}H_{68}N_{10}O_6Zn$ (monomer) 1088.46, found 2178.36 [dimer, $(M+H)^+$], 1089.56. [monomer, $(M+H)^+$]; UV-vis (toluene) [l_{max} nm (log*e*)] 366 (4.95), 615 (4.46), 670 (5.07), 700 (5.24).

2-(1-Methyl-2-imidazolynyl)-9(10),16(17),23(24)-tri-*tert*-butylphthalocyaninatozinc (**5**)

Imidazolynylphthalocyaninatozinc **5** (77 mg, 72%) was synthesized from 2-cyano-9(10),16(17),23(24)-tri-*tert*-butylphthalocyanatozinc (**5**)[1] and *N*-methylethylenediamine in a similar manner for the preparation of **4**: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) *d* 9.03-9.81 (br, 7H, Ar-H), 8.21-8.51 (br, 3H, Ar-H), 6.62-6.92 (br, 1H, Ar-H), 5.27-5.62 (br, 1 H, Ar-H), 1.71-2.31 (m, 32 H, *tert*-Bu and *N*-$\underline{Me}$ and Im-H), -0.09-0.31 (br, Im-H); MALDI-TOF MS: *m/z* calcd for $C_{96}H_{92}N_{20}Zn_2$ (dimer) 1652.64, $C_{48}H_{46}N_{10}Zn$ (monomer) 826.32, found 1653.65 (dimer, $[M+H]^+$), 827.15 (monomer, $[M+H]^+$); ESI-MS: m/z found 1653.35 (dimer, $[M+H]^+$), 827.32 (monomer, $[M+H]^+$); UV-vis (toluene) [l_{max}/nm (log*e*)] 353 (4.90), 617 (4.50), 673 (5.08), 700 (5.21).

2-(1-Methyl-2-imidazolyl)-9(10),16(17),23(24)-tri-*tert*-butylphthalocyaninatozinc (**2**)

Imidazolylphthalocyaninatozinc **2** (6.6 mg, 95%) was synthesized in a similar manner for the preparation of **1**:^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) *d* 9.03-9.87 (br, 7H, Ar-H), 8.18-8.51

(br, 3H, Ar-H), 6.70-7.20 (br, 1H, Ar-H), 5.22-5.80 (br, 2H, Ar-H, Im-H), 2.82-3.06 (br, 1H, Im-H), 2.23-2.61 (br, 3H, *N*-Me), 1.70-2.14 (m, 27H, *tert*-Bu); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS) *d* 157.2, 154.6, 152.9, 138.9, 136.6, 129.7, 127.2, 123.2, 122.5, 119.1, 118.9, 36.0, 32.2; MALDI-TOF MS: *m/z* calcd for $C_{96}H_{92}N_{20}Zn_2$ (dimer) 1648.61, $C_{48}H_{46}N_{10}Zn$ (monomer) 824.30, found 1649.89 (dimer, $[M+H]^+$), 825.46 (monomer, $[M+H]^+$); ESI-MS: *m/z* found 1649.29 (dimer, $[M+H]^+$), 825.12 (monomer, $[M+H]^+$); UV-vis (toluene) [λ_{max}/nm (log*e*)] 352 (4.80), 616 (4.46), 672 (5.08), 700 (5.20).

2-Cyano-9(10),16(17),23(24)-tri-*tert*-butylphthalocyaninatomagnesium (**6**)

4-Cyanophthalonitrile (70 mg, 0.46 mmol), 4-*tert*-butylphthalonitrile (512 mg, 2.78 mmol), and $MgCl_2$ (150 mg, 1.58 mmol) were dissolved in *n*-pentanol (9.0 mL). Three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene was added to the mixture, and the mixture was refluxed under N_2 for 30 h. After the mixture was concentrated under reduced pressure, the residue was pored into water, and extracted with chloroform. The organic layer was dried over Na_2SO_4, and purified by silica gel chromatography (eluent: $CHCl_3$ 100%, pyridine/$CHCl_3$ (1:100), then pyridine/$CHCl_3$/EtOAc (1:100:20)) to afford **6** (92 mg, 27% based on 4-cyanophthalonitrile): ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) *d* 8.14 (s, 1H, Ar-H), 8.05 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.89-7.57 (m, 9 H, Ar-H), 7.57-7.45 (br, 1H, Ar-H and Im-H), 1.38-1.32 (m, 27H, *tert*-butyl); MALDI-TOF MS: *m/z* calcd for $C_{45}H_{39}N_9Mg$ 729.32, found 729.32 (M^+); UV-vis (toluene) [λ_{max} nm (log*e*)] 357 (4.68), 609 (4.25), 637 (4.32), 671 (4.88), 693 (4.95).

2-(1-Methyl-2-imidazolyl)-9(10),16(17),23(24)-tri-*tert*-butylphthalocyaninatomagnesium (3)

Imidazolynylphthalocyaninatomagnesium **7** was synthesized from 2-cyano-9(10),16(17),23(24)-tri-*tert*-butylphthalocyaninatomagnesium (**6**) (11 mg, 15 μmol) and *N*-methylethylenediamine in a similar manner for the preparation of **4**. The crude **7** was used directly for next dehydrogenation. Imidazolylphthalocyanine **3** (6.7 mg, 57%, 2 steps) was synthesized in a similar manner for the preparation of **1**: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) *d* 9.98-8.88 (br, 7H, Ar-H), 8.59-8.11 (br, 3H, Ar-H), 7.22-6.86 (br, 1H, Ar-H), 5.87-5.40 (br, 2H, Ar-H, Im-H), 3.29-3.02 (br, 1H, Im-H), 2.75-2.36 (br, 3H, *N*-Me), 2.07-1.74 (m, 27H, *tert*-Bu); MALDI-TOF MS: *m/z* calcd for $C_{96}H_{92}N_{20}Zn_2$ (dimer) 1568.72, $C_{48}H_{46}N_{10}Zn$ (monomer) 784.36, found 1569.12 [dimer, $[M+H]^+$], 784.46 [monomer, M^+]; UV-vis (toluene) [l_{max}/nm (log$e$)] 352 (4.80), 616 (4.46), 672 (5.08), 700 (5.20).

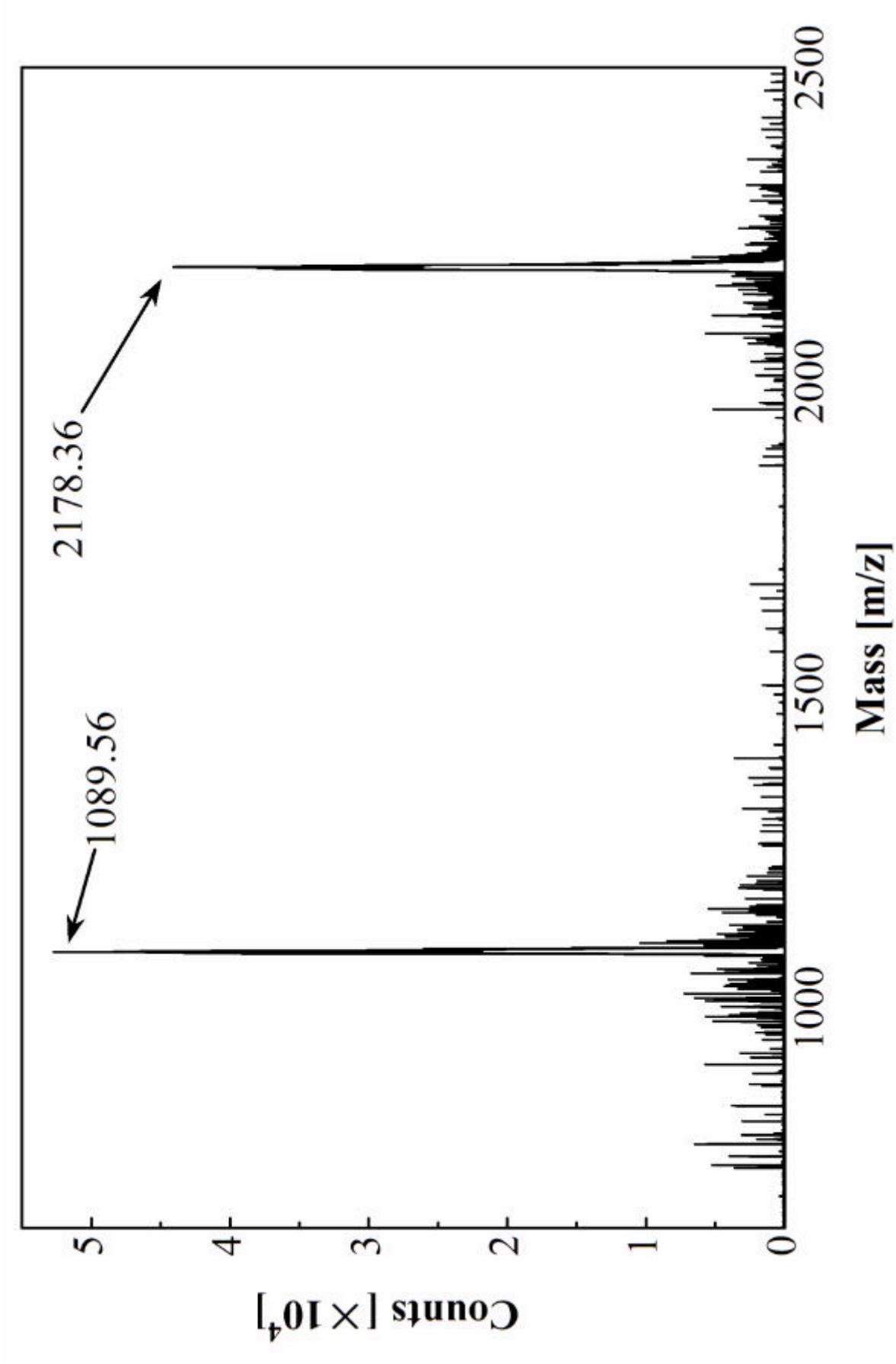


Figure S1. MALDI-TOF mass spectrum of **1 and [1]$_2$**.

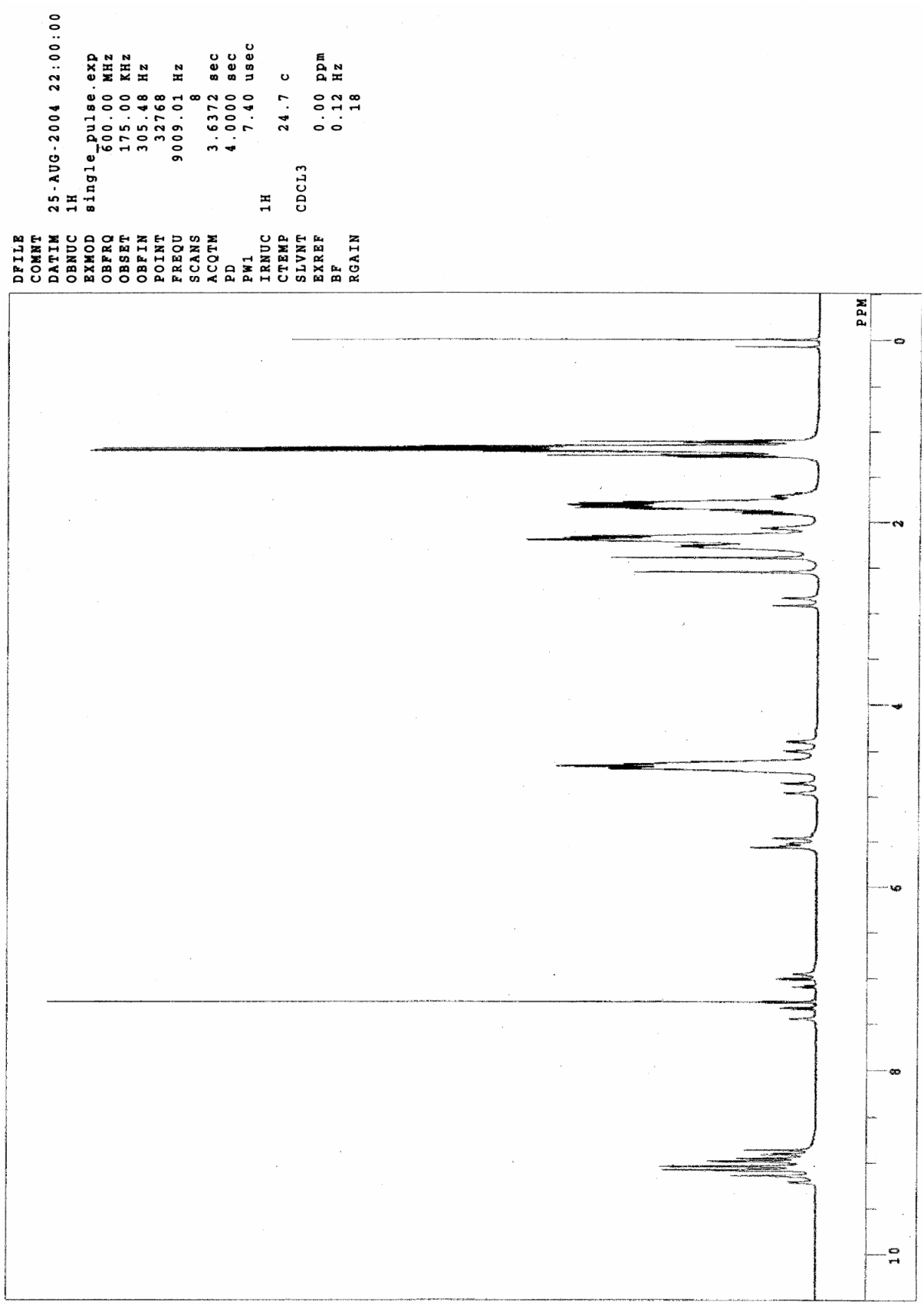


Figure S2. ^{1}H NMR spectrum of dimer **[1]$_2$** in $CDCl_3$.

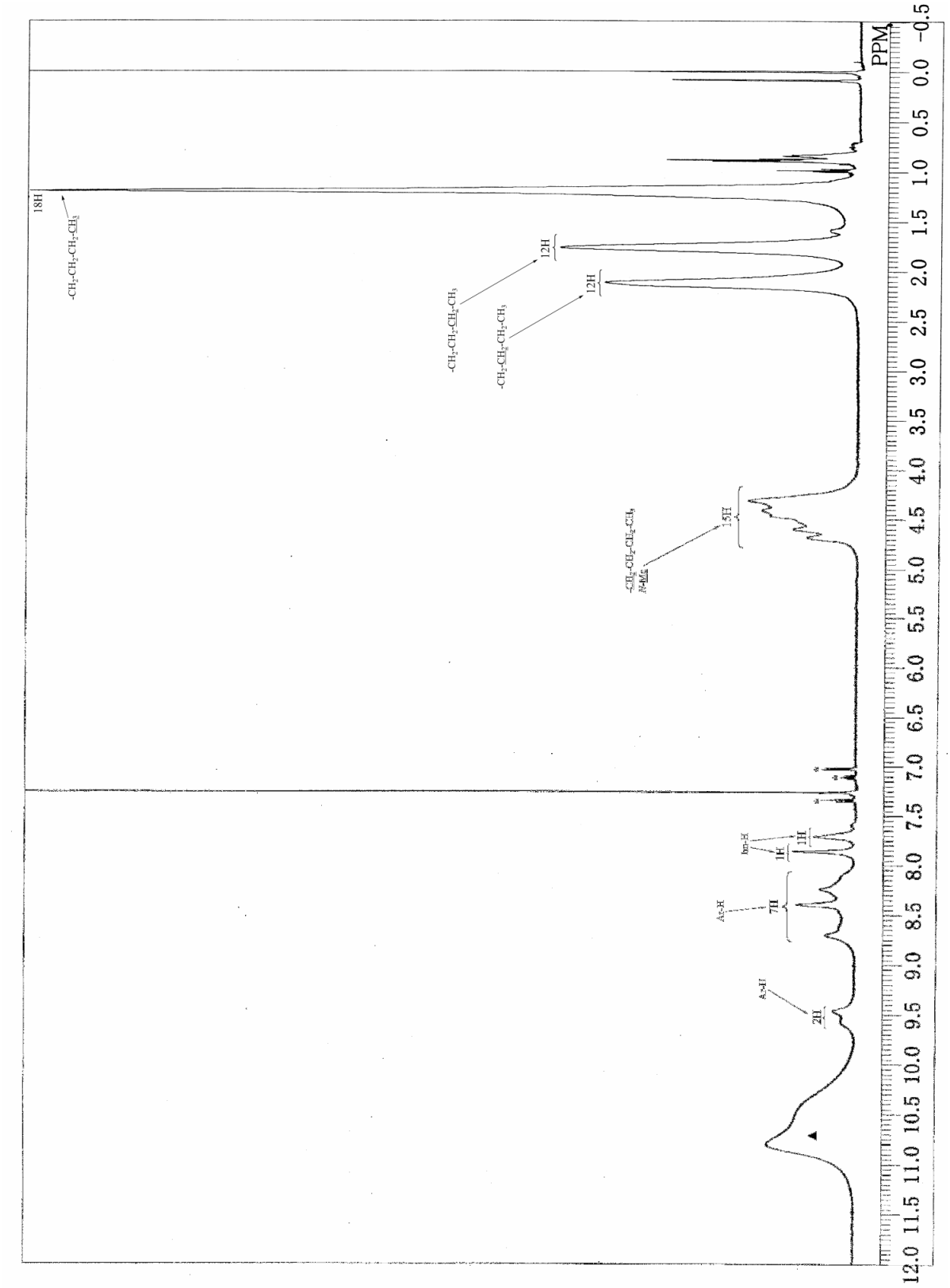


Figure S3. ^{1}H NMR spectrum of monomer **1** dissociated by the addition of 10% TFA. The asterisk and filled triangle denote the residual diphenylether used as solvent and TFA signals, respectively. The coordination dimer was robust even in the presence of pyridine or *N*-methylimidazole under the NMR condition, due to the high association constant. The coordination dimer was therefore dissociated into the corresponding monomer by protonation with addition of TFA for ^{1}H NMR measurement.

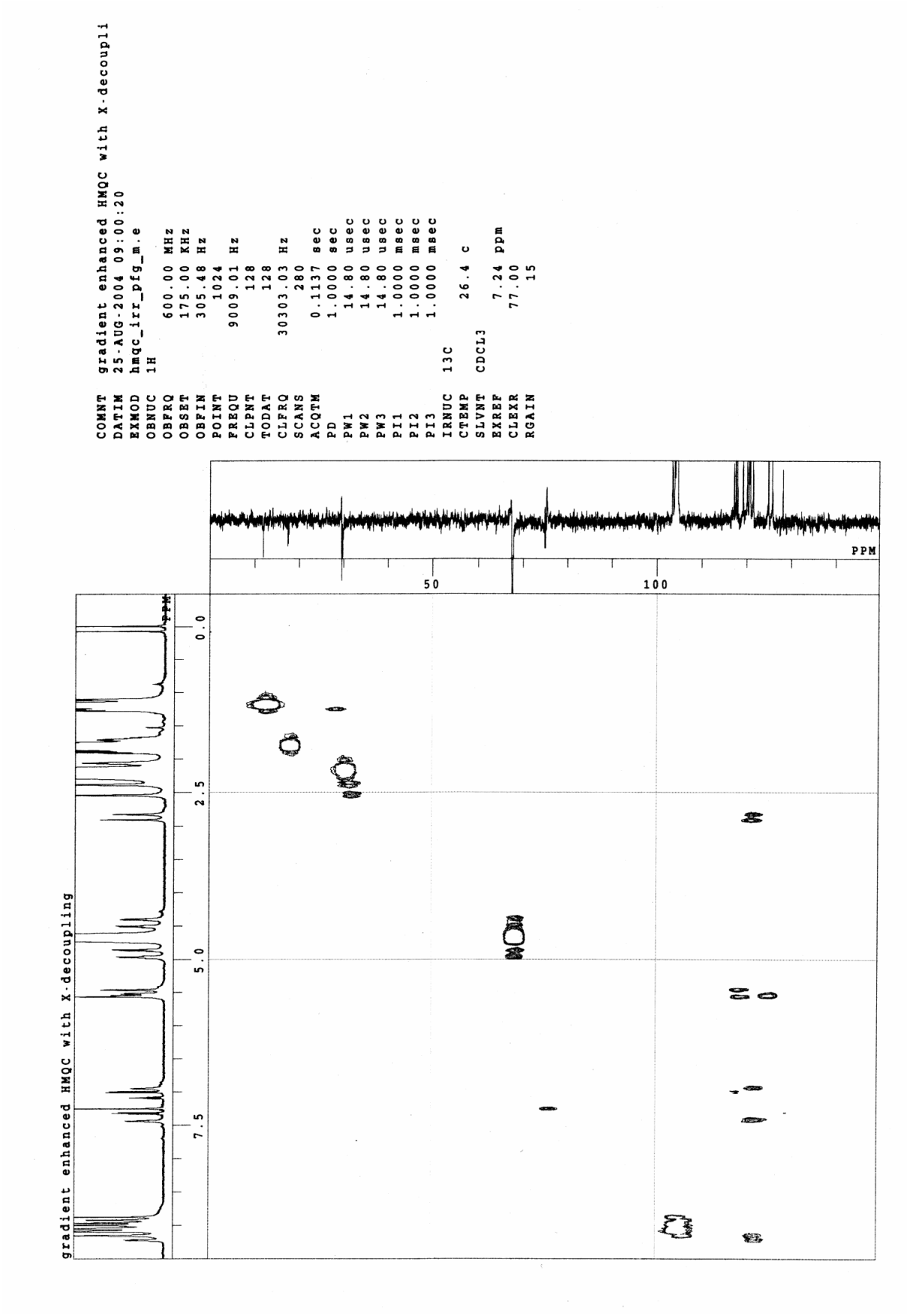


Figure S4. HMQC NMR spectrum of **[1]**$_2$ in $CDCl_3$.

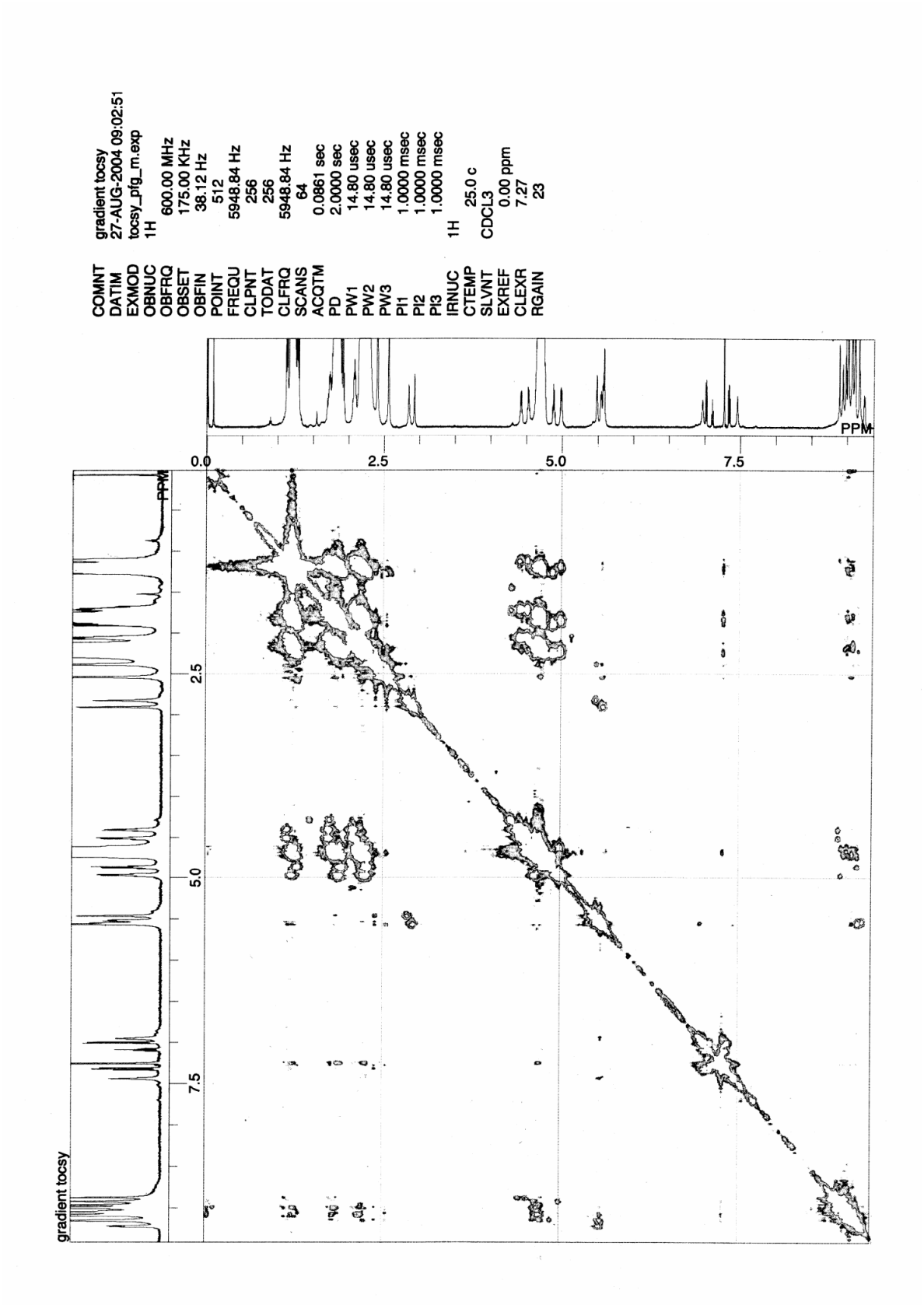


Figure S5. TOCSY NMR spectrum of **[1]**$_2$ in $CDCl_3$. Each set of correlating imidazolyl protons, i, j and k, was observed for the one set at 2.39, 2.83 and 5.47 ppm, and the other at 2.55, 2.91 and 5.57 ppm, respectively. In the phenyl part, f, g and h were likewise observed at (5.53, 9.16, and 6.96) and (5.55, 9.23, and 7.44) ppm, respectively.

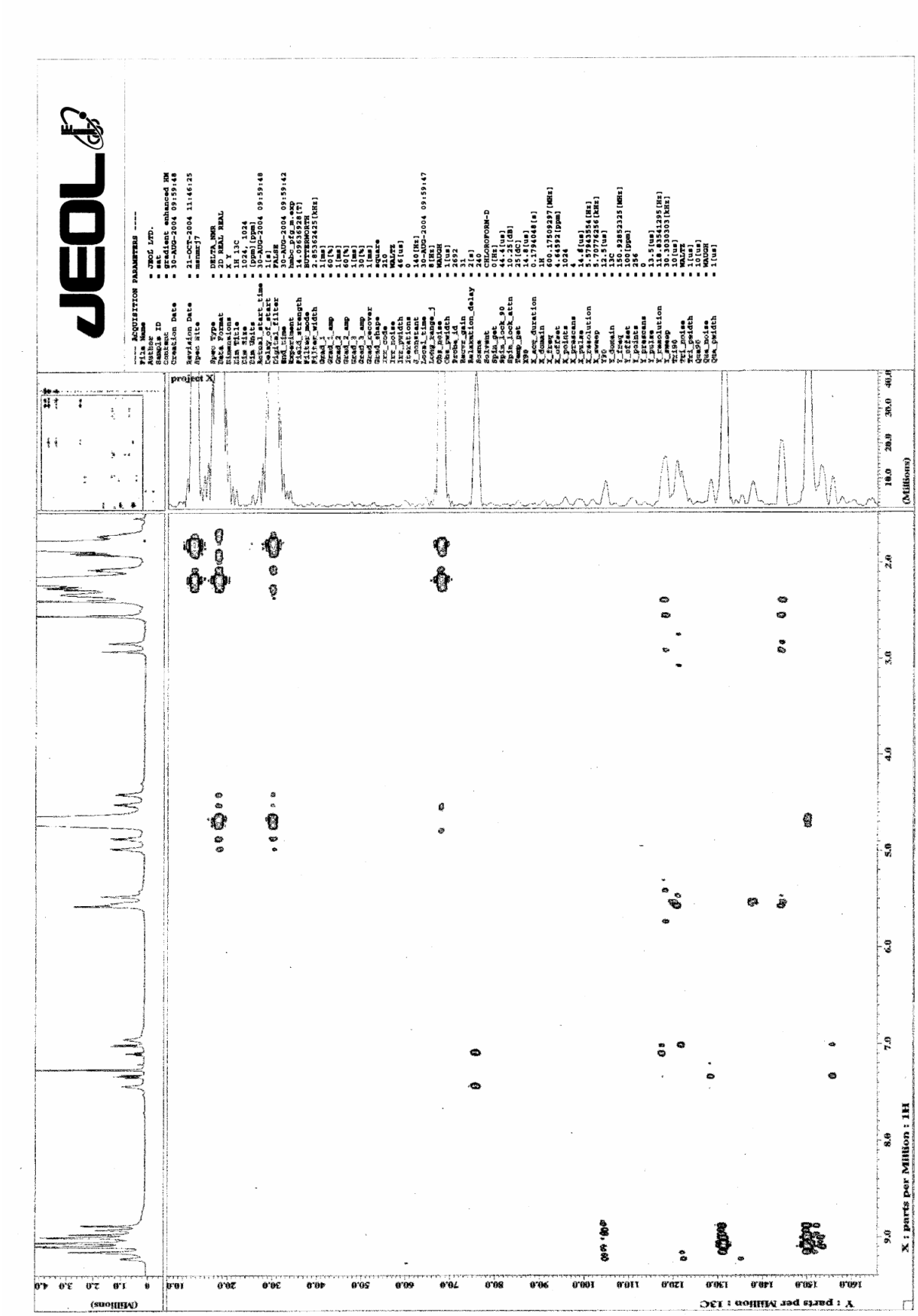


Figure S6. HMBC NMR spectrum of $[\mathbf{1}]_2$ in $CDCl_3$.

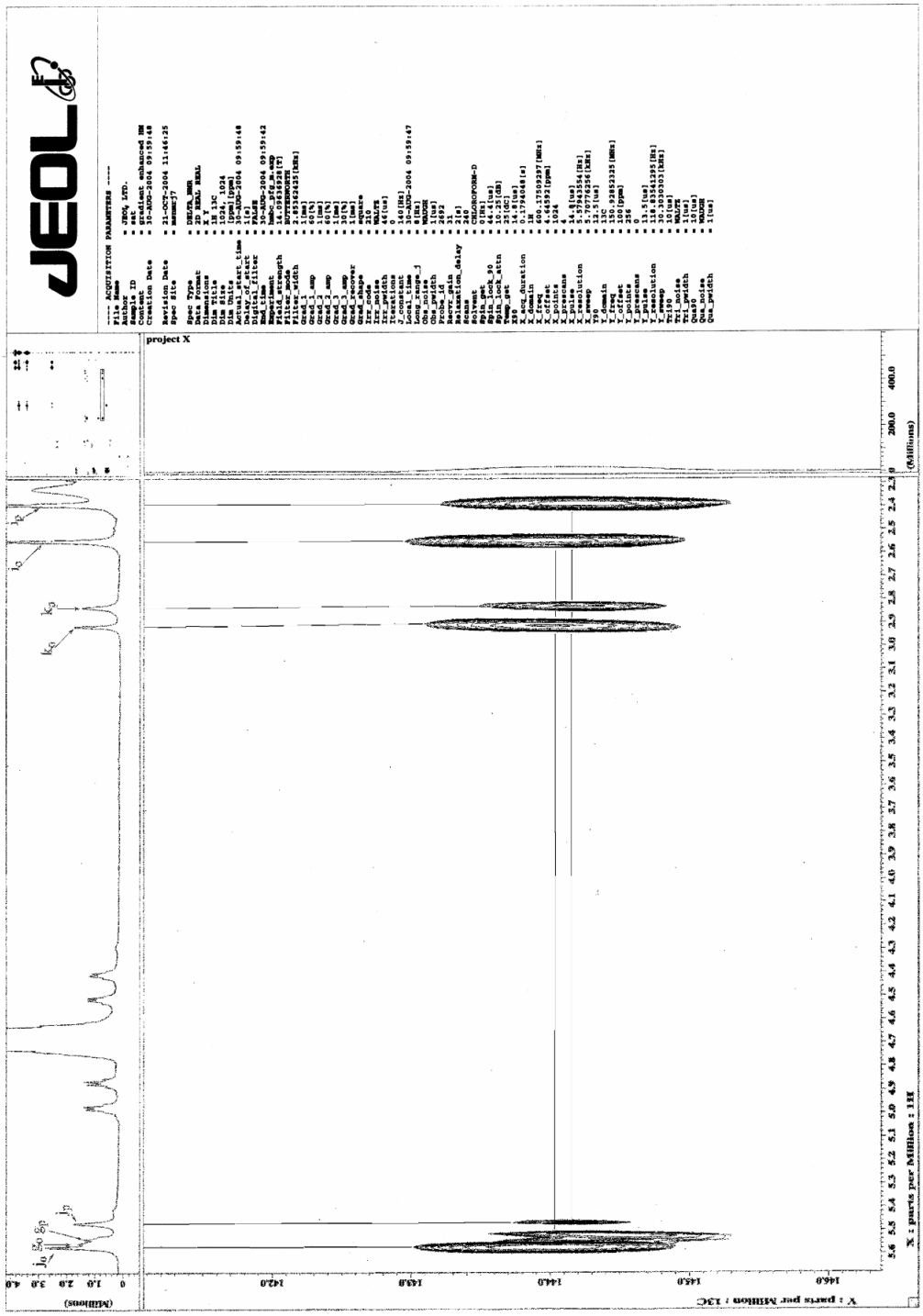


Figure S7. HMBC NMR spectrum of **[1]$_2$** in the range of (2.28 - 5.68 ppm) × (141.1 - 146.3 ppm). Correlations to the quaternary imidazolyl carbons (m, 143.98 and 144.22 ppm) were observed with protons g, i, j and k. Therefore, the two sets of f, g, h, i, j and k protons were assigned as shown in Figure 2.

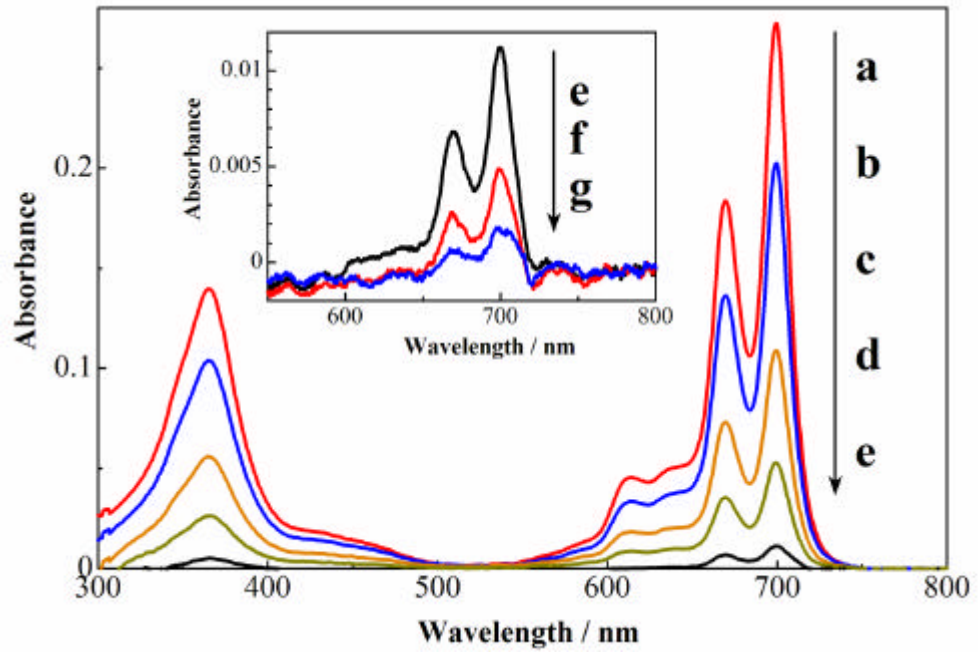


Figure S8. UV-vis spectra of **[1]$_2$** in toluene (light pathway: 10 cm). The arrow indicates the decrease of concentration of **[ImZnPc]$_2$** (as a monomer, **a**; 157, **b**; 116, **c**; 62.6, **d**; 30.4, **e**; 6.44, **f**; 2.82 and **g**; 1.03×10^{-9} M). Inset: Expanded absorption spectra of **e, f** and **g**.

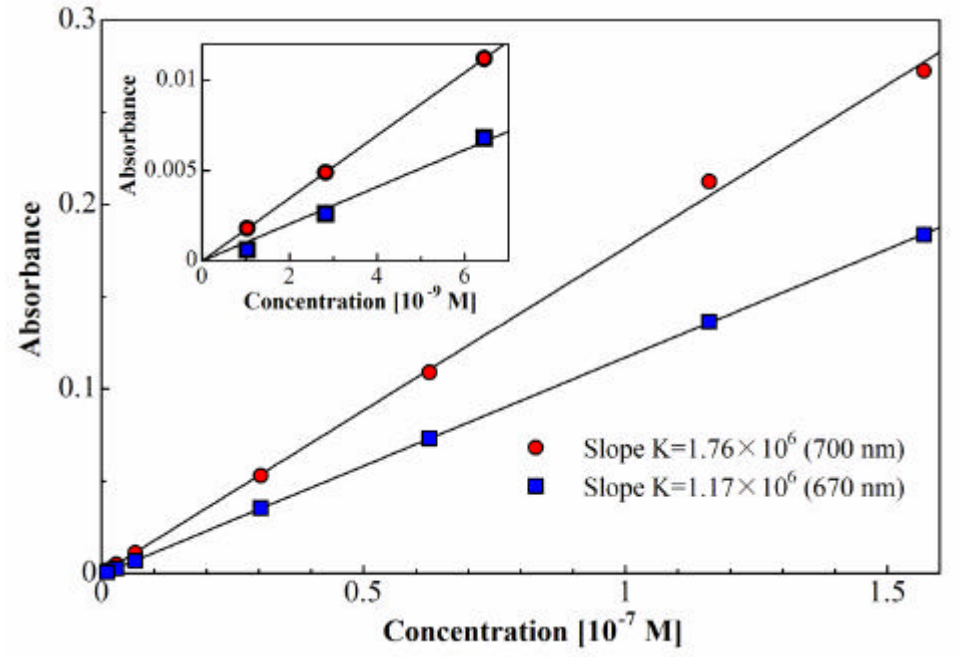


Figure S9. Relationship between absorbance at 700 (closed circle) and 670 nm (closed square), and concentration of **[1]$_2$** (as a monomer) from Figure S8. Beer's law is valid between 1.57×10^{-7} and 1.03×10^{-9} M, suggesting the structural robustness even at a nanomolar concentration.

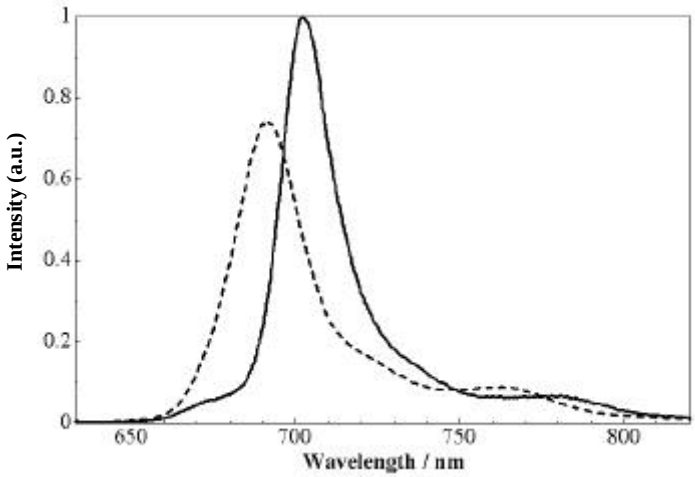
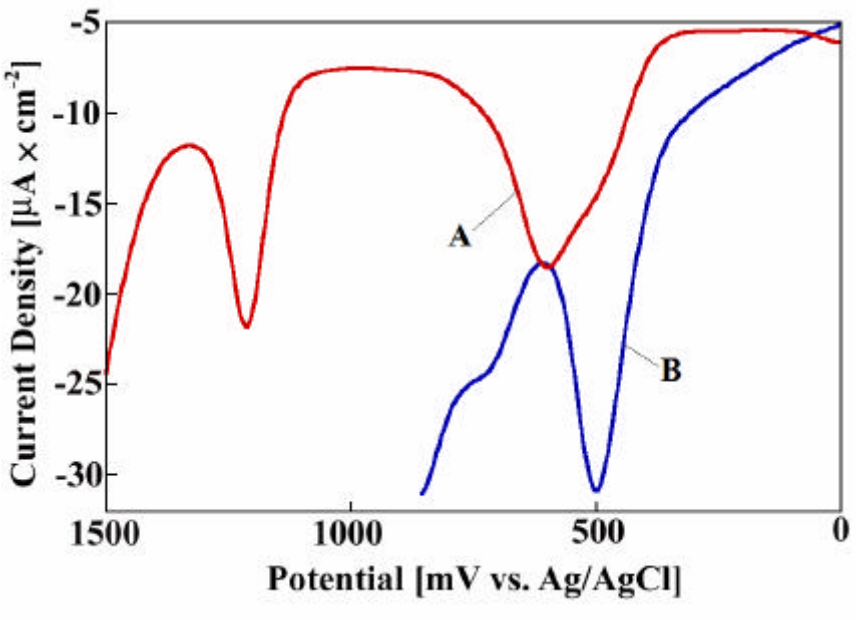
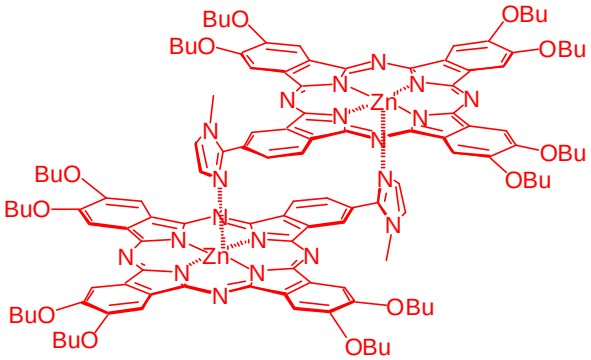
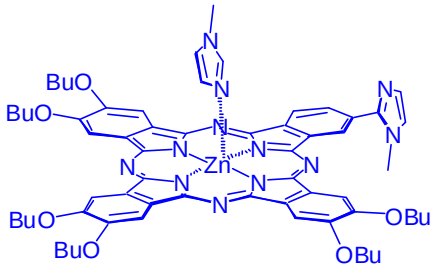


Figure S10. Fluorescence spectra of dimer **[1]$_2$** (solid line) and dissociated monomer **1-Im** (broken line) in toluene excited at 624 nm which is an isosbestic point of *N*-methylimidazole titration.





A: $(ImZnPc)_2$



B: ImZnPc-Im

Figure S11. Differential pulse voltammetry (DPV) of $\mathbf{[1]_2}$ (0.1 mM, as a monomer) in the absence (A) and presence (B) of *N*-methylimidazole (10^4 eq). Conditions: CH_2Cl_2, $^nBu_4N{\cdot}PF_6$ (0.1 M) as a supporting electrolyte, continuous Ar stream and 298 K. Differential pulse voltammetry (DPV) of $\mathbf{[1]_2}$ showed split oxidation waves at 510 and 619 mV for the phthalocyanine ring oxidation, corresponding to one and two electron oxidations from the dimer, respectively (***Figure S12***).

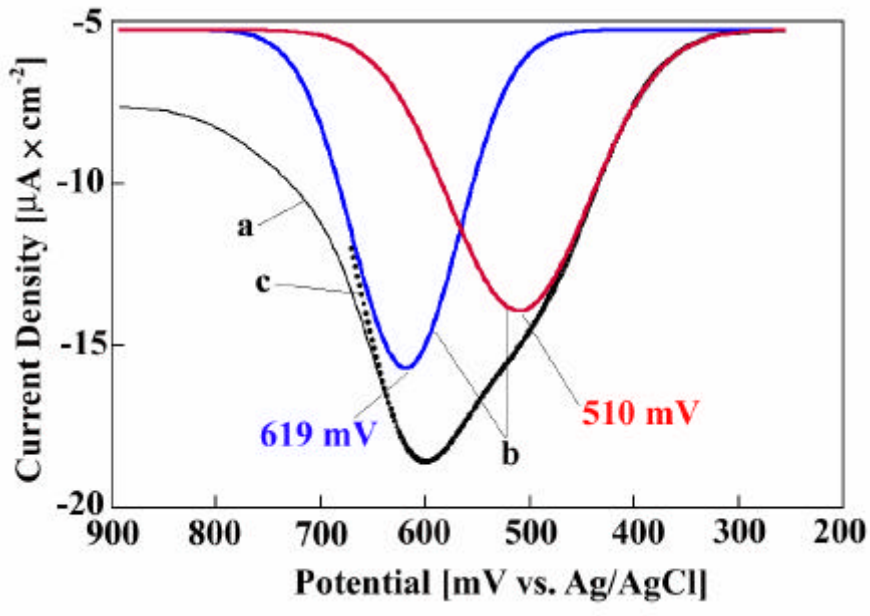


Figure S12. Peak-fitting analysis of DPV in Figure S10-A (200-900 mV). (a) Recorded data, (b) deconvoluted peaks (Gaussian, calculated by Origin® Peak Fitting Module Version 7), and (c) sum of the deconvoluted peaks.

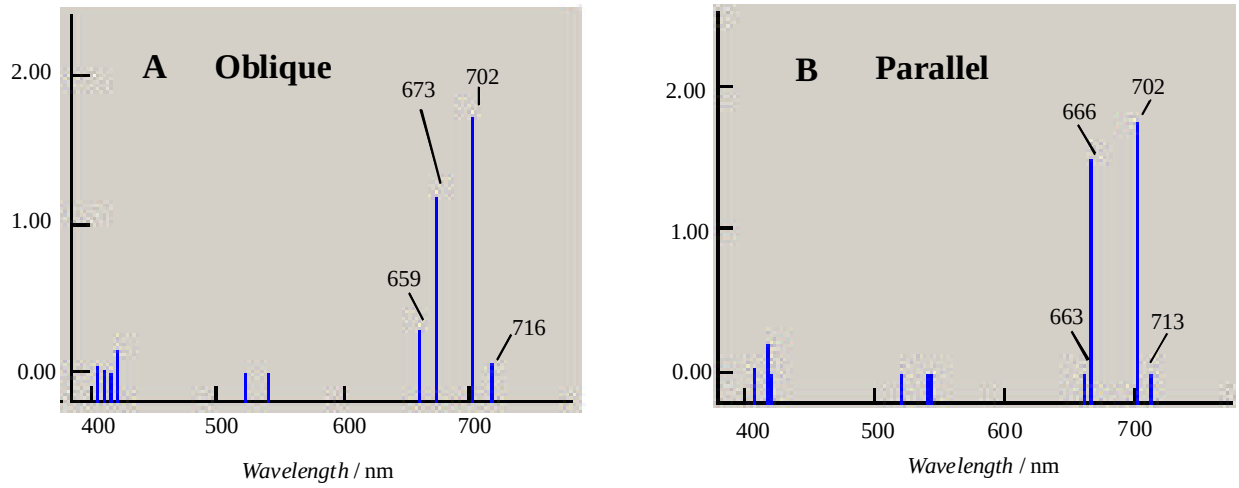


Figure S13. Electronic spectra of (A) oblique and (B) parallel calculated by INDO/S.

References

[1] K. Kameyama, A. Satake, Y. Kobuke, *Tetrahedron Lett.* **2004**, *45*, 7617-7620.

[2] T. Sauer, G. Wegner, *Mol. Cryst. Liq. Cryst.* **1988**, *162*, 97.