Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI) for

Organic Mixed Valency in Quadruple Hydrogen-bonded Triarylamine Dimers Bearing Ureido Pyrimidinedione Moieties

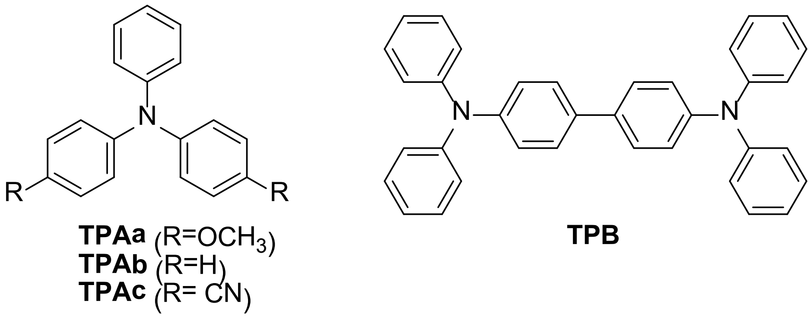
Keishiro Tahara,[a],* Tetsufumi Nakakita,[a] Shohei Katao,[a] and Jun-ichi Kikuchi[a],*

[a]Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5, Takayama, Ikoma, Nara 6300192, Japan.

Contents

1. Materials and general measurements

All solvents and chemicals used in the synthesis were of reagent grade and were used without further purification. A CH_2Cl_2 solution of $SbCl_5$ (1.0 M) was purchased from Sigma-Aldridge, Inc. 4,4'-Dimethoxydipehnylamine, **TPB** (tetraphenylbenzidine) and **TPAb** (triphenylamine) were purchased from TCI (Chart S1). 2-Amino-5,5-dibutyl-1*H*-pyrimidine-4,6-dione,[S1] 4-aminotriphenylamine,[S2] 4,4'-dicyanodipehnylamine,[S3] **TPAa**[S4] and **TPAc**[S5] were synthesized according to previously reported procedures. The UV-vis-NIR absorption spectra were measured on a JASCO V-670 spectrometer at room temperature. The ^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded using JEOL JNM-ECP400 and JNM-ECA600 spectrometers installed at the Nara Institute of Science and Technology; tetramethylsilane (TMS) was used as an internal standard (0 ppm) for ^{1}H- and ^{13}C{^{1}H}-NMR analysis. The ESI-MS and EI-MS were obtained using JEOL JMS-T100CS and JMS-700 MStation spectrometers, respectively. The MALDI-TOF-MS were obtained using a Bruker Autoflex II spectrometer. Elemental analyses were performed using a Perkin Elmer 2400 II CHNS/O elemental analyzer.



TPAa ($R=OCH_3$)
TPAb (R=H)
TPAc (R= CN)

TPB

Chart S1. Structures of reference compounds.

2. Synthesis and characterization of compounds

Synthesis of 1-(5,5-dibutyl-1,4,5,6-tetrahydro-4,6-dioxopyrimidin-2-yl)-3-{4-(diphenylamino)phenyl}urea (1b)

Triphosgene (0.74 g, 2.5 mmol) was dissolved in 15 mL of dry dichloromethane and the solution was cooled to 0 °C. To the solution a solution of 4-aminotriphenylamine[S2] (0.65 g, 2.5 mmol) and 1.38 mL of triethylamine in dry dichloromethane (15 mL) was added. After 10 min of stirring at 0 °C, 12.5 mL of dry pyridine was added. Then, 2-Amino-5,5-dibutyl-1*H*-pyrimidine-4,6-dione (0.60 g, 2.5 mmol)[S1] was added. The reaction mixture was refluxed at 50 °C and filtered. The filtrate was concentrated to dryness. The resulting solid was dissolved in dichloromethane and washed with water. After drying the organic layer over Na_2SO_4, the solution was concentrated to dryness.

The target product **1b** was purified by silica-gel column chromatography using chloroform as the eluent. Yield: 0.48 g (36%). ^{1}H-NMR (400 MHz, $\mathrm{CDCl_3}$, ppm): δ = 0.85 (t, J = 7.4 Hz, 6H, $\mathrm{-C\underline{H_3}}$), 1.26 (m, 8H, $\mathrm{-C\underline{H_2}C\underline{H_2}-}$), 2.01 (t, J = 8.2 Hz, 4H, $\mathrm{-C\underline{H_2}C(CO)(CO)C\underline{H_2}-}$), 7.00 (m, 2H, $\mathrm{-C(N)C(H)C(H)C(\underline{H})-}$), 7.09 (m, 6H, $\mathrm{-C(N)\underline{C}(H)C(H)C(H)-}$, $\mathrm{-C(NH)C(H)C(\underline{H})C(N)-}$), 7.23 (m, 4H, $\mathrm{-C(N)C(H)C(\underline{H})C(H)-}$), 7.54 (m, 2H, $\mathrm{-C(NH)C(\underline{H})C(H)C(N)-}$), 10.33, 11.23 (s, 1H, $\mathrm{-N(\underline{H})C(O)N(\underline{H})-}$), 12.75 (s, 1H, $\mathrm{-C(O)N(\underline{H})C(NH)N-}$) (Fig. S6). ^{13}C-NMR (150 MHz, $\mathrm{CDCl_3}$, ppm): δ = 13.70 ($\mathrm{-\underline{C}H_3}$), 22.67, 27.30 ($\mathrm{-\underline{C}H_2\underline{C}H_2-}$), 39.42 ($\mathrm{-\underline{C}H_2C(CO)(CO)\underline{C}H_2-}$), 58.12 ($\mathrm{-CH_2\underline{C}(CO)(CO)CH_2-}$), 121.25 ($\mathrm{-C(NH)\underline{C}(H)C(H)C(N)-}$), 122.66 ($\mathrm{-C(N)C(H)C(H)\underline{C}(H)-}$), 123.95 ($\mathrm{-C(N)\underline{C}(H)C(H)C(H)-}$), 124.81 ($\mathrm{-C(NH)C(H)\underline{C}(H)C(N)-}$), 129.23 ($\mathrm{-C(N)C(H)\underline{C}(H)C(H)-}$), 132.61, 144.41 ($\mathrm{-\underline{C}(NH)C(H)C(H)\underline{C}(N)-}$), 147.74 ($\mathrm{-\underline{C}(N)C(H)C(H)C(H)-}$), 155.38, 156.22 ($\mathrm{-N\underline{C}N(H)N(H)\underline{C}(O)N(H)-}$), 171.88, 180.76 ($\mathrm{-CH_2C(\underline{C}O)(\underline{C}O)CH_2-}$) (Fig. S7). HR-ESI-MS (m/z): calc. for $\mathrm{C_{31}H_{35}N_5NaO_3}$ ($\mathrm{[M+Na]^+}$): 548.26376. Found: 548.26321 (Fig. S1).

Synthesis of 4,4'-dimethoxy-4"-nitrotriphenylamine

The target compound was synthesized according to a procedure for aromatic nucleophilic substitution reactions reported elsewhere.[S2] 4,4'-Dimethoxydipehnylamine (2.29 g, 10.0 mmol) was added to a mixture of sodium hydride (0.375 g, 15.6 mmol) and dry *N*, *N*-dimethylacetamide (10 mL). The reaction mixture was stirred at room temperature for 1 h and cooled to 0 °C. 4-Fluoronitrobenzene (1.69 g, 12.0 mmol) in dry *N*, *N*-dimethylacetamide (10 mL) was added dropwise to this mixture. After the addition was completed, the mixture was stirred at 100 °C for 3 h. Then the reaction mixture was cooled to room temperature and poured into a cold dilute hydrochloric acid solution. The resulting solid was corrected by filtration and recrystallized from ethanol. Yield: 1.88 g (54%). The NMR data were consistent with those previously reported.[S6]

Synthesis of 1-(5,5-dibutyl-1,4,5,6-tetrahydro-4,6-dioxopyrimidin-2-yl)-3-{4-[bis(4-methoxyphenyl)amino]phenyl}urea (1a)

The mixture of 4,4'-dimethoxy-4"-nitrotriphenylamine (1.17 g, 3.33 mmol) and palladium on activated carbon (Pd/C) (0.048 g) in dry ethanol (10 mL) was refluxed for 1h. Hydrazine monohydrate (1.0 mL) was added dropwise and refluxed overnight. After Pd/C was removed by filtration, the filtrate was concentrated to dryness. The resulting white solid (1.07 g) was identified as 4-amino-4',4"-dimethoxytriphenylamine by NMR comparisons to reported data.[S6] The reaction proceeded quantitatively and this compounds was used without further purification. Following the similar procedure for synthesis of **1b** and using the crude product of 4-amino-4’,4”-dimethoxytriphenylamine (1.07 g), the target compound was synthesized and purified. Yield: 0.560 g (29%). ^{1}H-NMR (600 MHz, CDCl$_3$, ppm): δ = 0.85 (t, J = 7.5 Hz, 6H, -C$\underline{H}_3$), 1.27 (m, 8H, -C$\underline{H}_2$C$\underline{H}_2$-), 2.00 (t, J = 8.1 Hz, 4H, -C$\underline{H}_2$C(CO)(CO)C$\underline{H}_2$-), 3.79 (s, 6H, -OC$\underline{H}_3$), 6.82 (m, 4H, -C(N)C(H)C($\underline{H}$)C(OCH$_3$)-), 6.95 (m, 2H, -C(N)C($\underline{H}$)C(H)C(NH)-), 7.04 (m, 4H, -C(N)C($\underline{H}$)C(H)C(OCH$_3$)-), 7.45 (m, 2H, -C(N)C(H)C($\underline{H}$)C(NH)-), 10.47, 11.42 (s, 1H, -N($\underline{H}$)C(O)N($\underline{H}$)-), 12.81 (s, 1H, -C(O)N($\underline{H}$)C(NH)N-) (Fig. S4). ^{13}C-NMR (150 MHz, CDCl$_3$, ppm): δ = 13.71 (-$\underline{C}$H$_3$), 22.69, 27.30 (m, 8H, -$\underline{C}$H$_2\underline{C}$H$_2$-), 39.44 (-$\underline{C}$H$_2$C(CO)(CO)$\underline{C}$H$_2$-), 55.50 (-O$\underline{C}$H$_3$), 58.10 (-CH$_2\underline{C}$(CO)(CO)CH$_2$-), 114.66 (-C(N)C(H)$\underline{C}$(H)C(OCH$_3$)-), 121.24 (-C(N)C(H)$\underline{C}$(H)C(NH)-), 121.63 (-C(N)$\underline{C}$(H)C(H)C(NH)-), 126.11(-C(N)$\underline{C}$(H)C(H)C(OCH$_3$)-), 130.70, 141.12, 145.57, 155.40, 155.64, 156.01, 172.02, 180.82 (Fig. S5). HR-ESI-MS (m/z): calc. for $C_{33}H_{39}N_5O_5$ ([M]$^+$): 585.29512. Found: 585.29491.

Synthesis of 4,4’-dicyano-4”-nitrotriphenylamine

Following the similar procedures for synthesis of 4,4’-dimethoxy-4”-nitrotriphenylamine and using 4,4’-dicyanodipehnylamine,[S3] the target compound was synthesized. Yield: 4.78 g (94%). The NMR data were consistent with those previously reported.[S7]

Synthesis of 4-amino-4’,4”-dicyanotriphenylamine

The mixture of 4,4’-dicyano-4”-nitrotriphenylamine (2.55 g, 7.50 mmol) and palladium on activated carbon (Pd/C) (0.1087 g) in dry ethanol (20 mL) was refluxed for 1h. Hydrazine monohydrate (2.5 mL) was added dropwise and refluxed overnight. After Pd/C was removed by filtration, the filtrate was concentrated to dryness. The resulting solid was reprecipitated from chloroform/hexane to afford the target product as a yellow solid. Yield: 1.99 g (85.5%). ^{1}H-NMR (600 MHz, CDCl$_3$, ppm): δ= 3.79 (br, 2H, -N$\underline{H}_2$), 6.70 (m, 2H, -C(N)C(H)C($\underline{H}$)C(NH$_2$)-), 6.93 (m, 2H, -C(N)C($\underline{H}$)C(H)C(NH$_2$)-), 7.08 (m, 2H, -C(N)C($\underline{H}$)C(H)C(≡N)-), 7.50 (m, 2H, -C(N)C(H)C($\underline{H}$)C(≡N)-) (Fig. S2). ^{13}C-NMR (150 MHz, CDCl$_3$, ppm): δ= 104.88, 116.42 (-C(N)C(H)$\underline{C}$(H)C(NH$_2$)-), 119.14 (-$\underline{C}$≡N), 121.92 (-C(N)$\underline{C}$(H)C(H)C(≡N)-), 128.93(-C(N)$\underline{C}$(H)C(H)C(NH$_2$)-), 133.39 (-C(N)C(H)$\underline{C}$(H)C(≡N)-), 135.35, 145.49, 150.36 (Fig. S3). HR-EI-MS (m/z): calc. for $C_{20}H_{14}N_4$ ([M]$^+$): 310.1219. Found: 310.1217.

Synthesis of 1-(5,5-dibutyl-1,4,5,6-tetrahydro-4,6-dioxopyrimidin-2-yl)-3-{4-[bis(4-cyanophenyl)amino]phenyl}urea (1c)

Following the similar procedures for synthesis of **1b** and using 4-amino-4’,4”-dicyanotriphenylamine, **1c** was synthesized which was purified by silica-gel column chromatography using chloroform as the eluent. Yield: 0.97 g (56%). ^{1}H-NMR (600 MHz, $CDCl_3$, ppm): $\delta = 0.86$ (t, $J = 7.2$ Hz, 6H, $-C\underline{H_3}$), 1.30 (m, 8H, $-C\underline{H_2}C\underline{H_2}-$), 2.04 (m, 4H, $-C\underline{H_2}C(CO)(CO)C\underline{H_2}-$), 7.13 (m, 6H, $-C(N)C(\underline{H})C(H)C(NH)-$, $-C(N)C(\underline{H})C(H)C(\equiv N)-$), 7.54 (m, 4H, $-C(N)C(H)C(\underline{H})C(\equiv N)-$), 7.73 (m, 2H, $-C(N)C(\underline{H})C(H)C(NH)-$), 10.57, 11.34 (s, 1H, $-N(\underline{H})C(O)N(\underline{H})-$), 12.77 (s, 1H, $-C(O)N(\underline{H})C(NH)N-$) (Fig. S8). ^{13}C-NMR (150 MHz, $CDCl_3$, ppm): $\delta = 13.69$ ($-\underline{C}H_3$), 22.65 , 27.29 ($-\underline{C}H_2\underline{C}H_2-$), 39.35 ($-\underline{C}H_2C(CO)(CO)\underline{C}H_2-$), 58.10 ($-CH_2\underline{C}(CO)(CO)CH_2-$), 105.86, 118.88 ($-\underline{C}\equiv N$), 121.71 ($C(N)C(H)\underline{C}(H)C(NH)-$), 122.76 ($-C(N)\underline{C}(H)C(H)C(\equiv N)-$), 127.61 ($C(N)\underline{C}(H)C(H)C(NH)-$), 133.57 ($-C(N)C(H)\underline{C}(H)C(\equiv N)-$), 136.23, 141.02, 150.07, 154.71, 157.24, 171.34, 179.80 (Fig. S9). HR-ESI-MS (m/z): calc. for $C_{33}H_{33}N_7NaO_3$ ($[M+Na]^+$): 598.25426. Found: 598.25478.

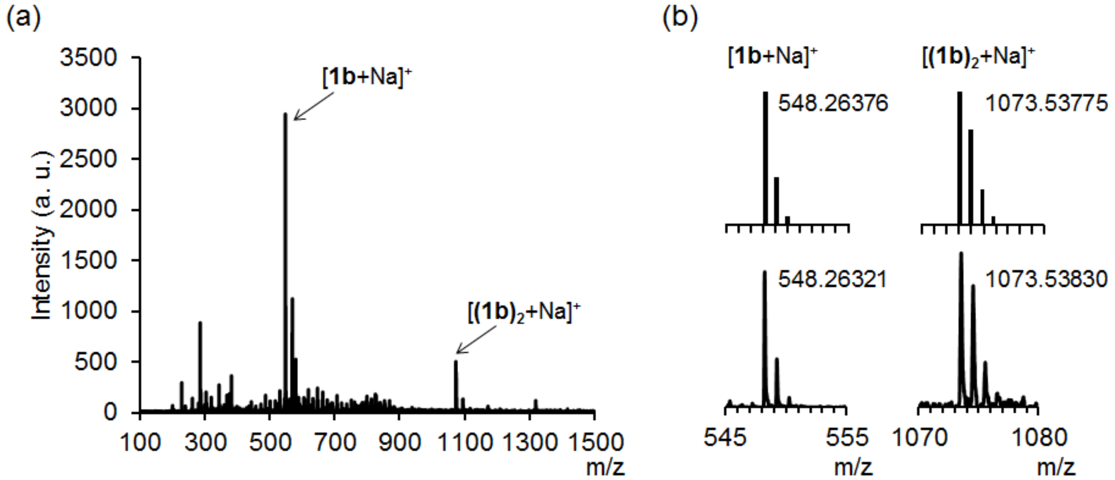


Fig. S1 (a) ESI-MS of **1b**. (b) Experimental (bottom) and theoretical (top) isotopic distributions for [**1b**+Na]$^+$ and [(**1b**)$_2$+Na]$^+$.

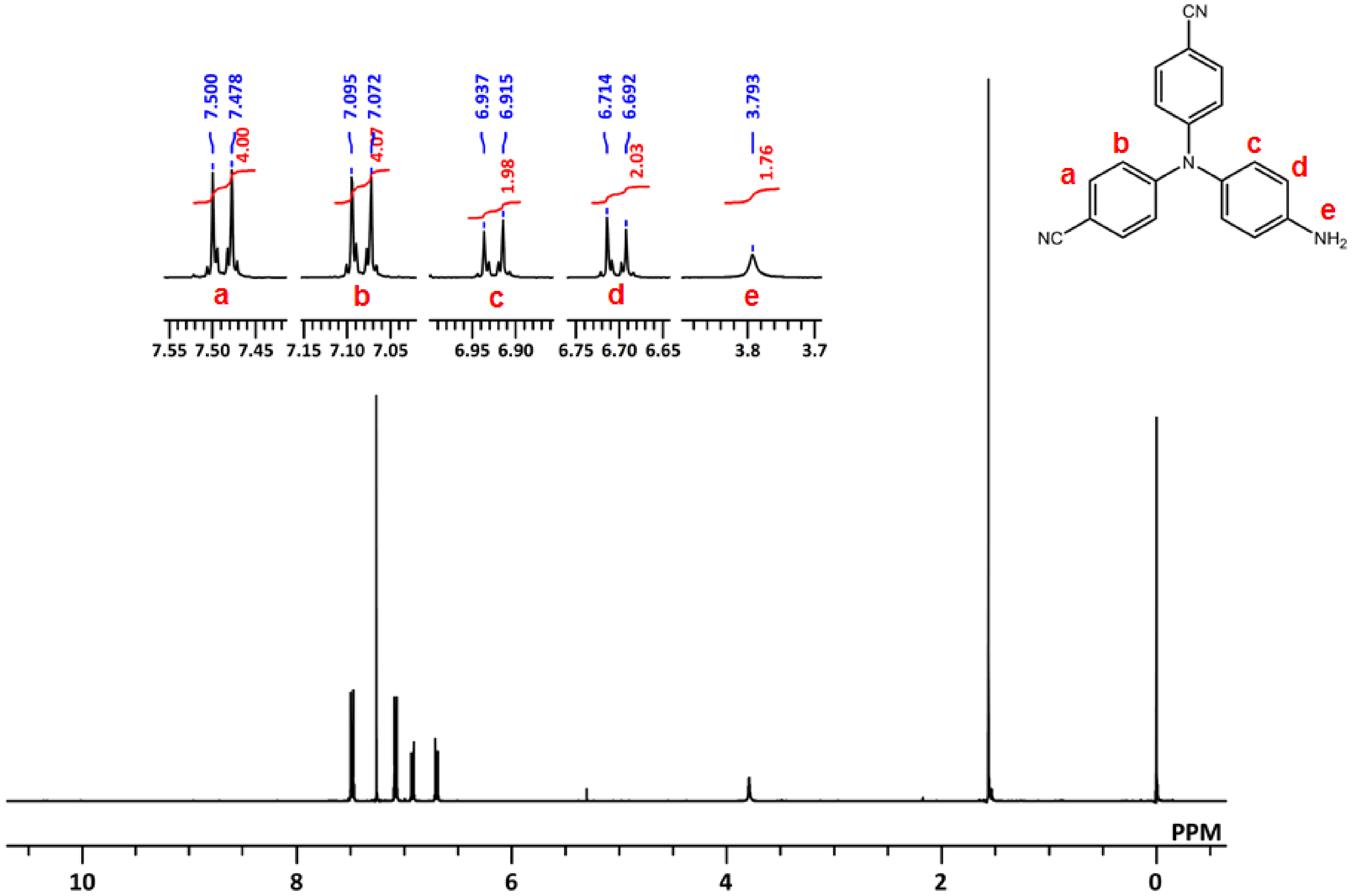


Fig. S2 ^{1}H-NMR spectrum of 4-amino-4’,4”-dicyanotriphenylamine in $CDCl_3$ (400 MHz).

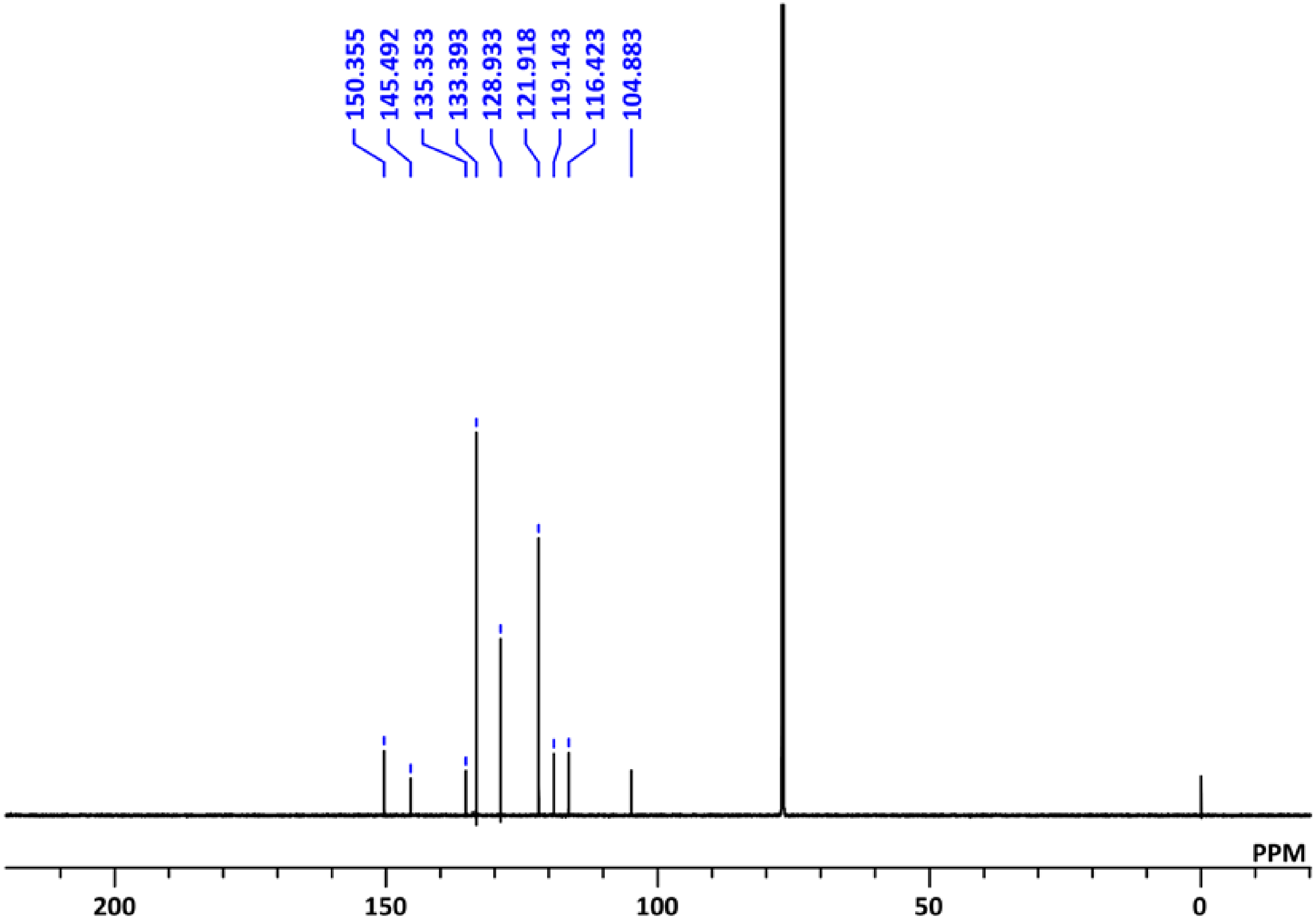


Fig. S3 ^{13}C-NMR spectrum of 4-amino-4’,4’’-dicyanotriphenylamine in $CDCl_3$ (150 MHz).

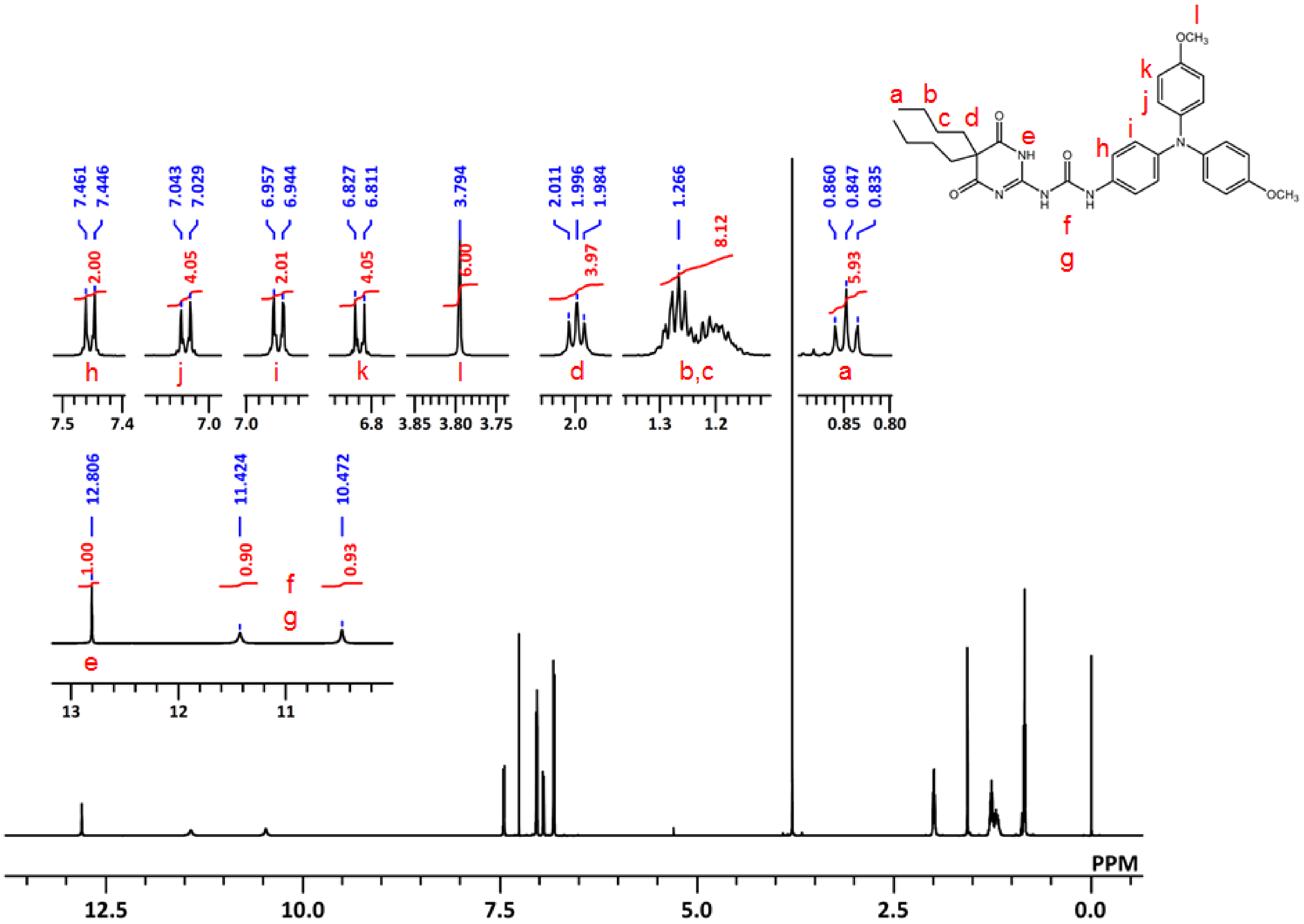


Fig. S4 ^{1}H-NMR spectrum of **1a** in $CDCl_3$ (600 MHz).

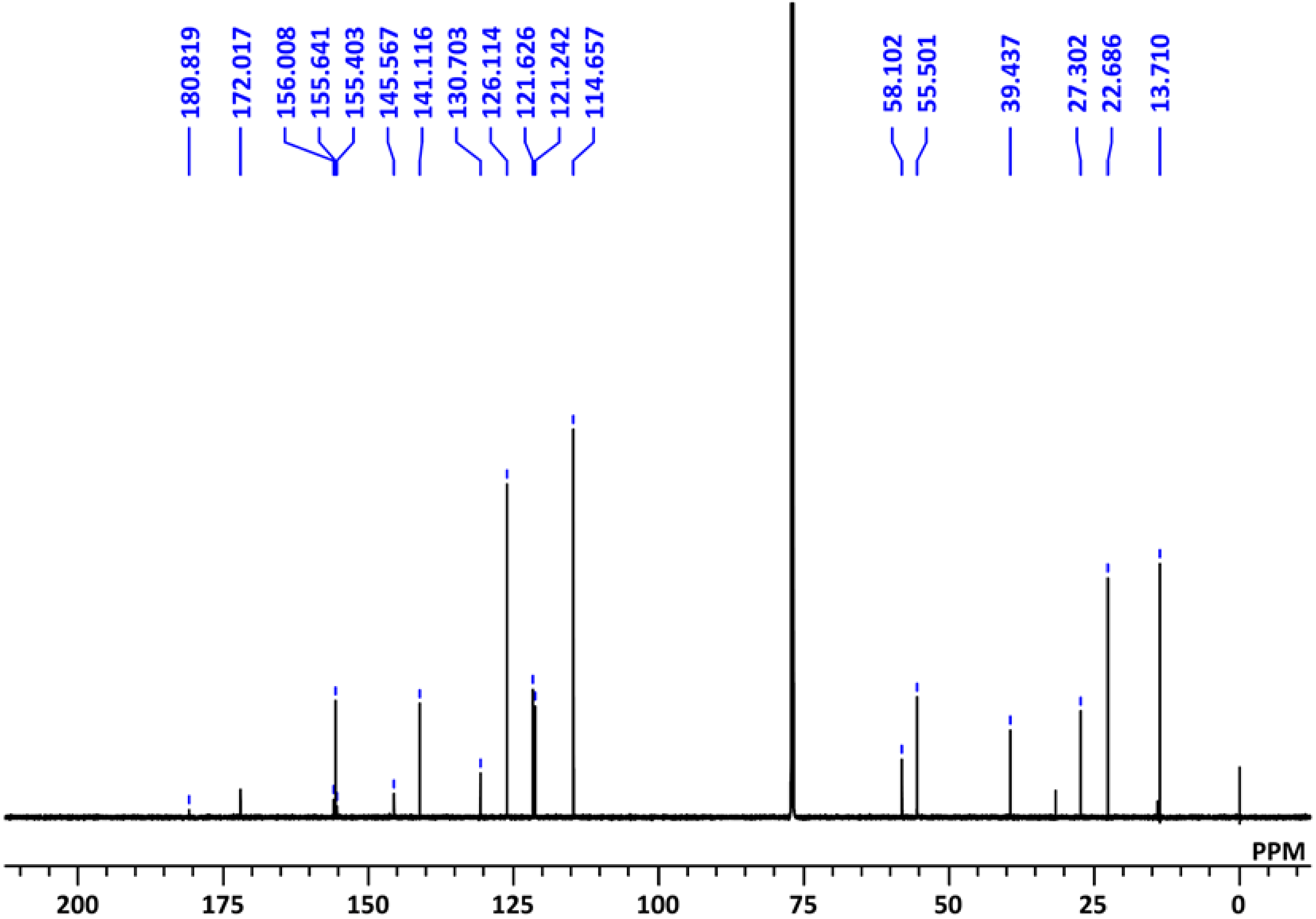


Fig. S5 ^{13}C-NMR spectrum of **1a** in $CDCl_3$ (150 MHz).

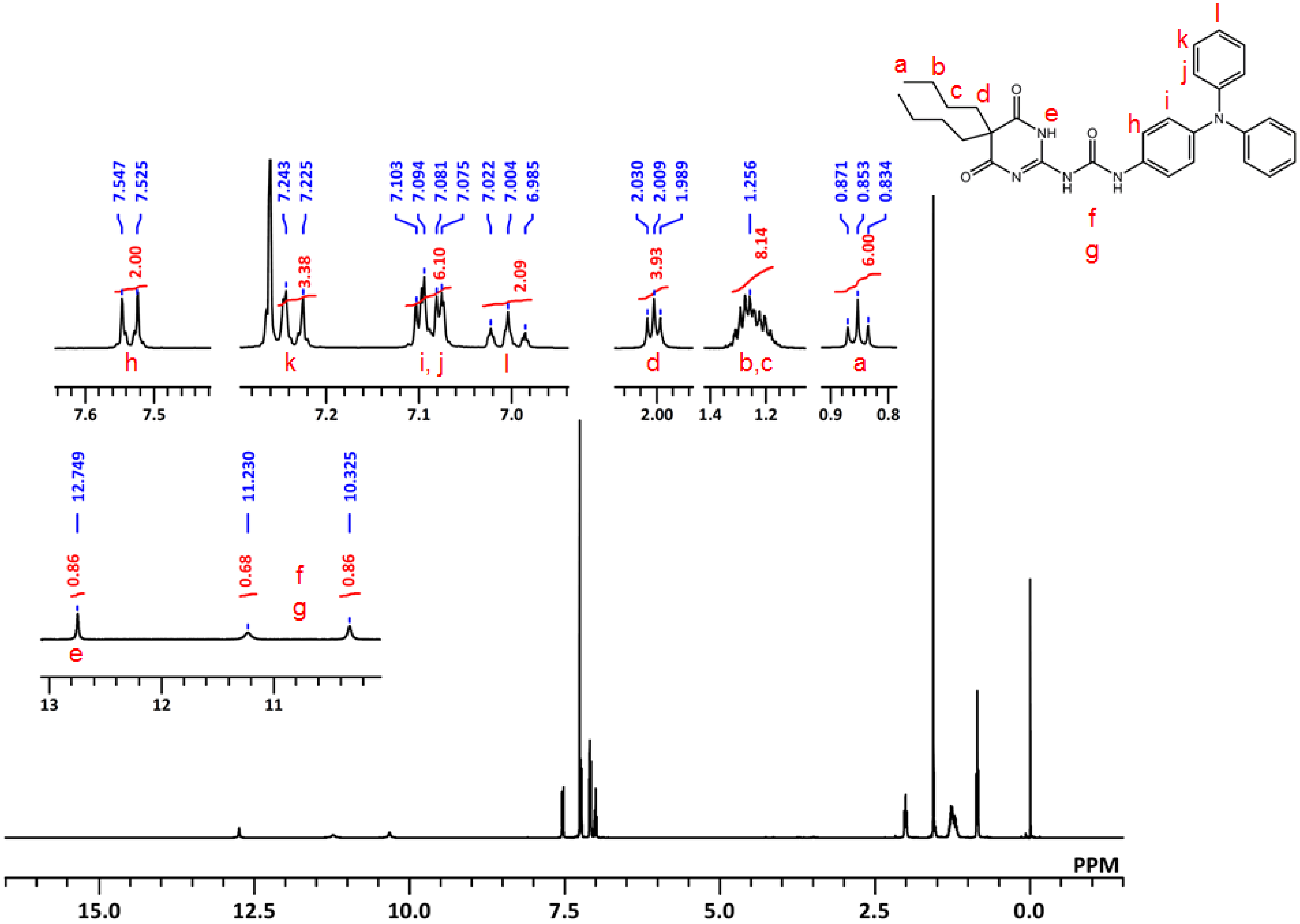


Fig. S6 ^{1}H-NMR spectrum of **1b** in $CDCl_3$ (400 MHz).

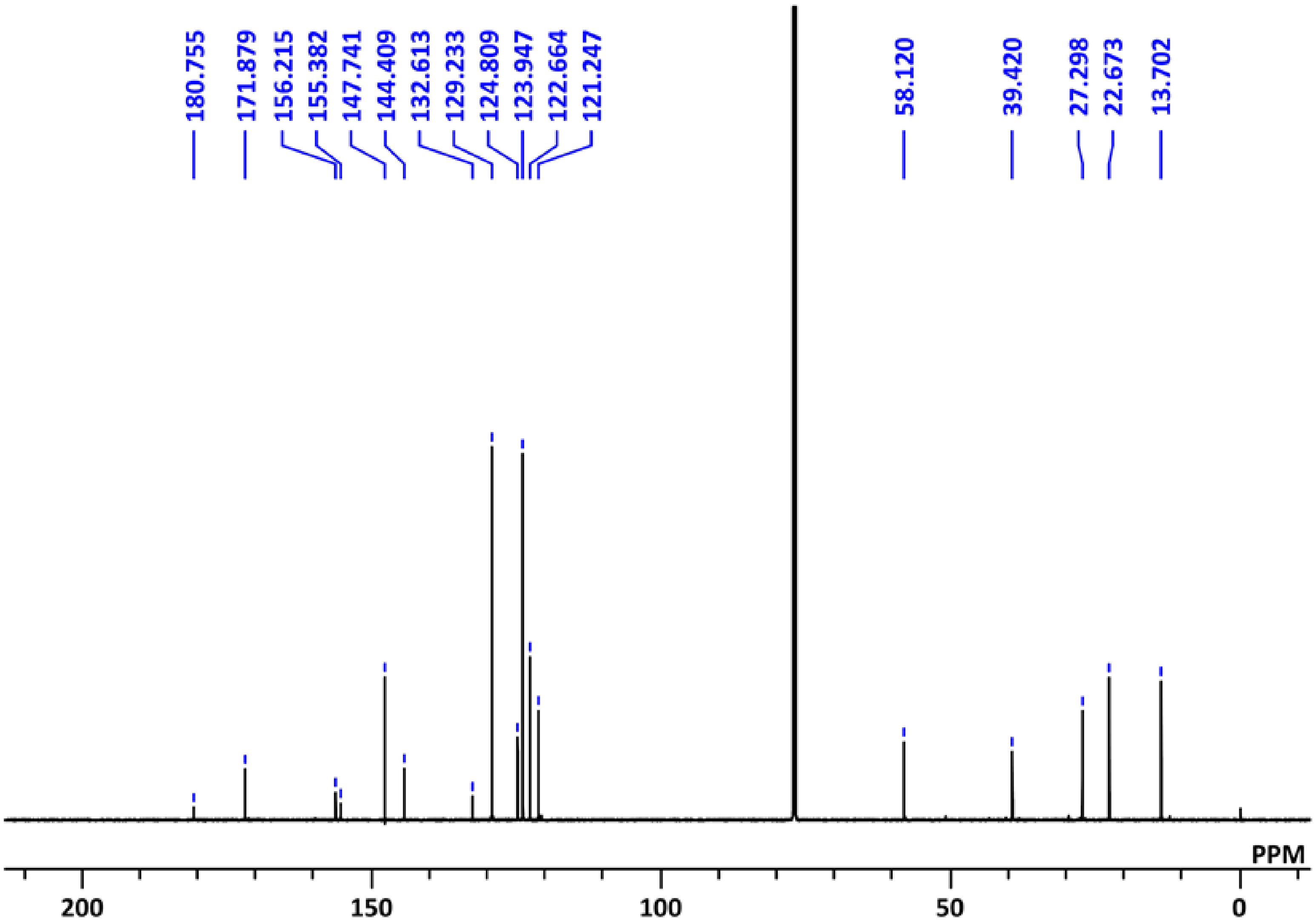


Fig. S7 ^{13}C-NMR spectrum of **1b** in CDCl$_3$ (150 MHz).

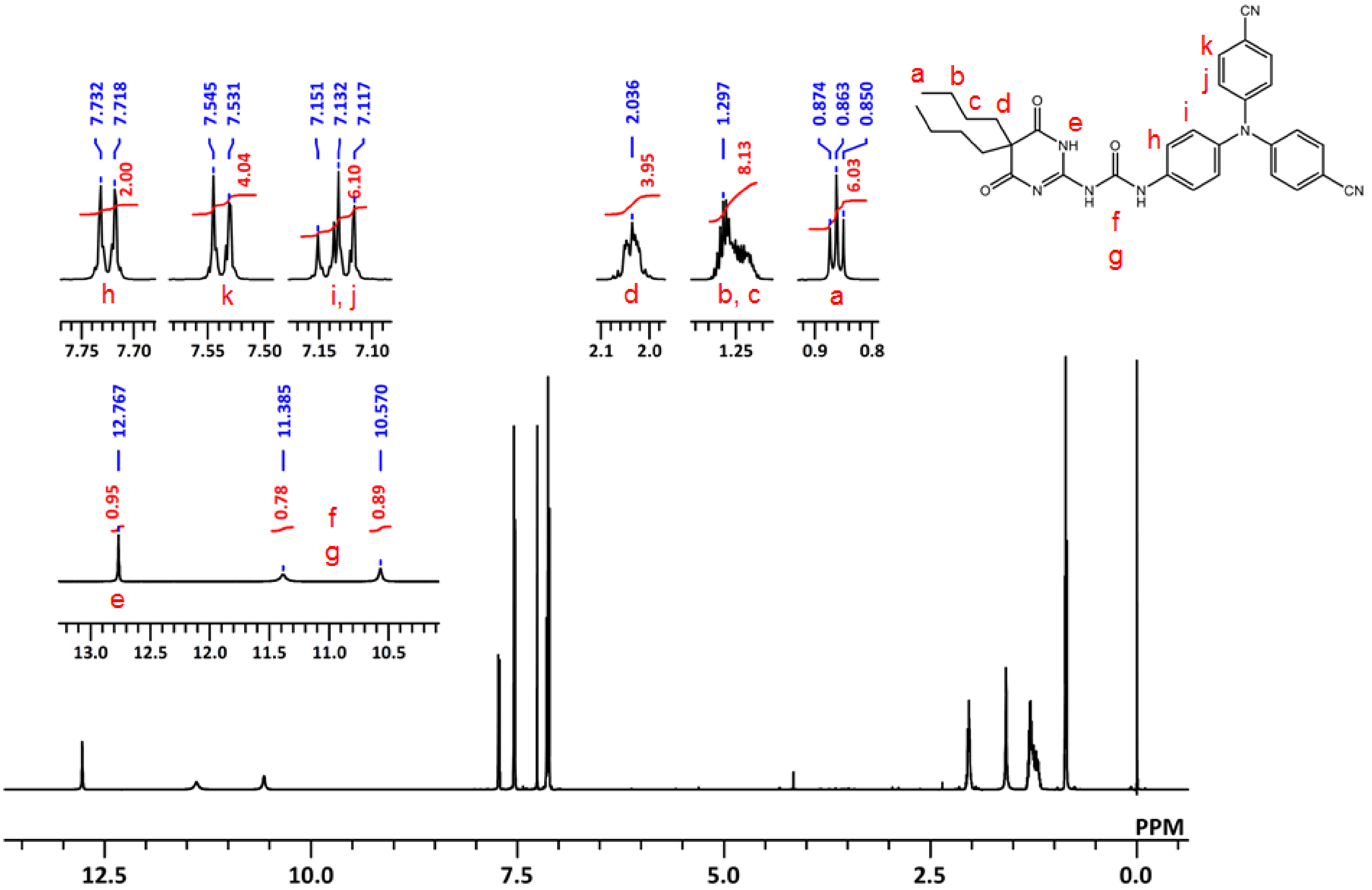


Fig. S8 ^{1}H-NMR spectrum of **1c** in $CDCl_3$ (600 MHz).

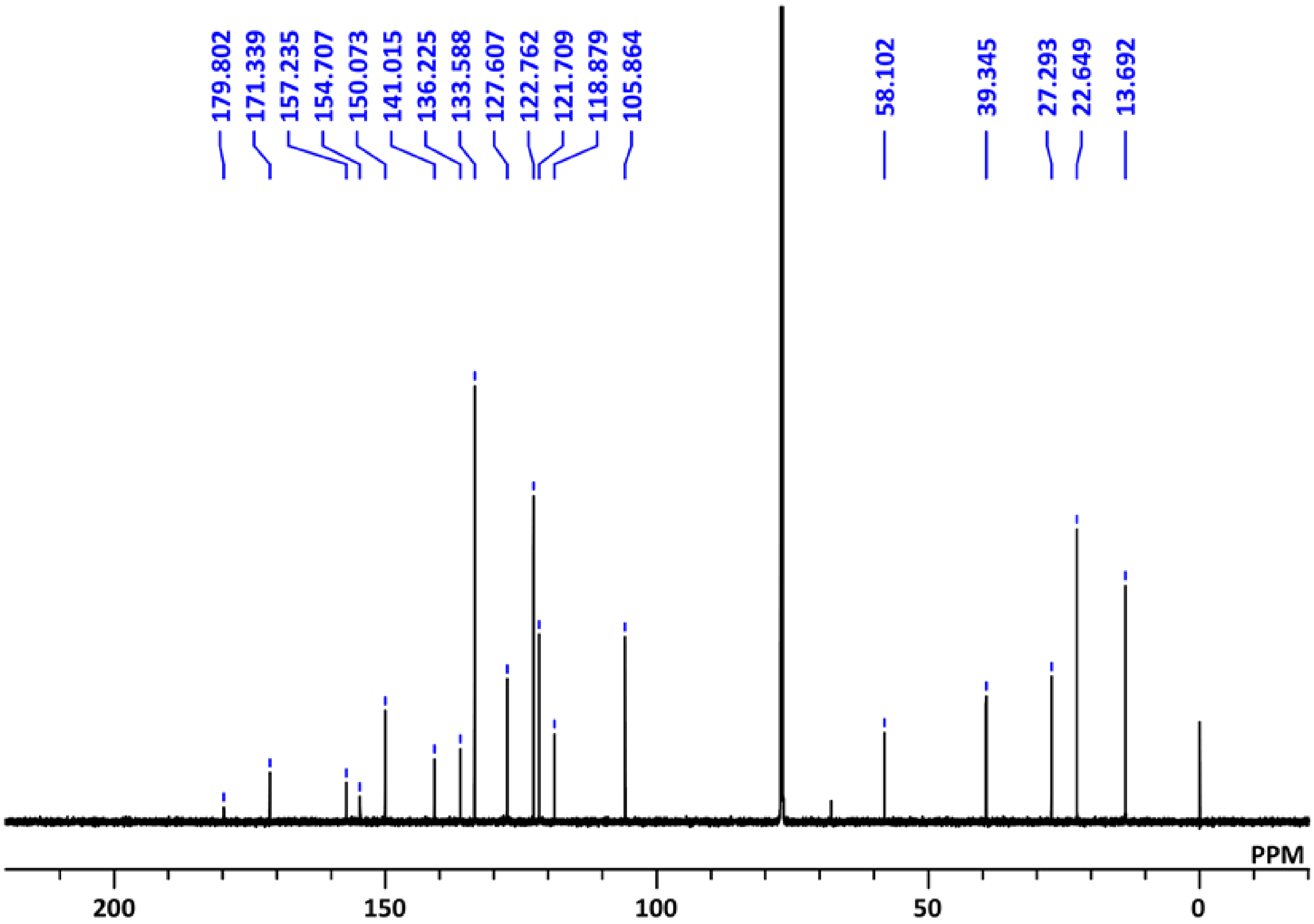


Fig. S9 ^{13}C-NMR spectrum of **1c** in $CDCl_3$ (150 MHz).

3. Single crystal X-ray diffraction (XRD) analysis

Single crystals of **1a** and **1b** suitable for XRD analysis were obtained by diffusion of hexane into chloroform solutions containing **1a** and **1b**, respectively, at ambient temperature. Data were collected with a Rigaku ValiMax RAPID RA-Micro7HFM using Mo Kα radiation at −150 °C. The diffraction data were processed with RAPID AUTO on a Rigaku program, and the structures were solved by direct methods and refined on F^2 by full-matrix least-squares using CrystalStructure and SHELXL-97 (Table S1). CCDC 989917 and 989918 contains the supplementary crystallographic data for **1a** and **1b** in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

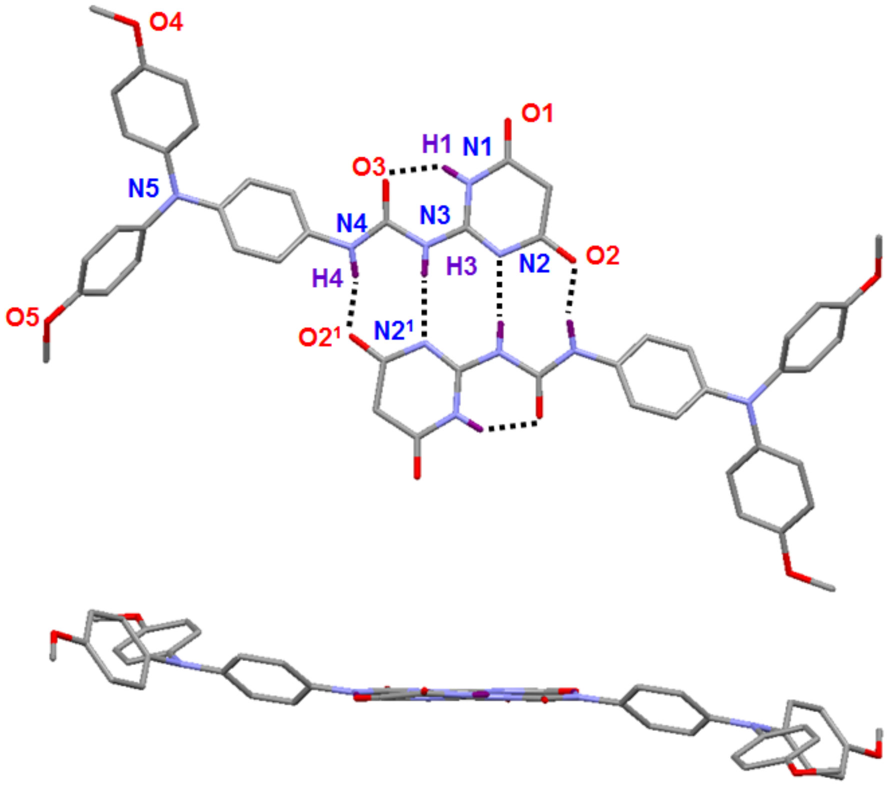


Fig. S10 Crystal structures of **1a**. Intra- and intermolecular hydrogen bonds are indicated as dotted lines; *n*-butyl substituents and hydrogen atoms are omitted for clarity except for N-H hydrogens (purple).

Table S1. Summary of crystallographic data and refinement parameters for **1a** and **1b**.

	1a	**1b**
empirical formula	$C_{33}H_{39}N_5O_5$	$C_{31}H_{35}N_5O_3$
formula weight	585.70	525.65
crystal dimensions (mm)	0.150 ×0.130 × 0.120	0.150 × 0.130 × 0.020
crystal system	triclinic	monoclinic
crystal habit, color	yellow, block	yellow, platelet
space group	P-1 (#2)	C2/c (#15)
temp (°C)	–150	–150
a (Å)	10.6611(4)	35.7967(9)
b (Å)	10.8302(3)	8.8766(2)
c (Å)	14.7696(4)	17.1376(4)
α	100.5167(7)	90
β (deg)	110.9923(7)	99.2802(7)
γ	91.6911(7)	90
V (Å^3)	1557.02(8)	5374.3(3)
Z	2	8
ρ_{calcd} (g cm^{-3})	1.249	1.299
F(000)	624.00	2240.00
μ (MoK_α) (cm^{-1})	0.853	0.854
$2\phi_{\mathrm{max}}$ (deg)	50.7	55.0
GOF	1.084	1.094
R1[a]	0.0677	0.0679
wR2[b]	0.1802	0.1919
$\Delta\rho_{\mathrm{max}}/\Delta\rho_{\mathrm{min}}$ (e/Å^3)	1.59/–0.40	0.86/–0.38

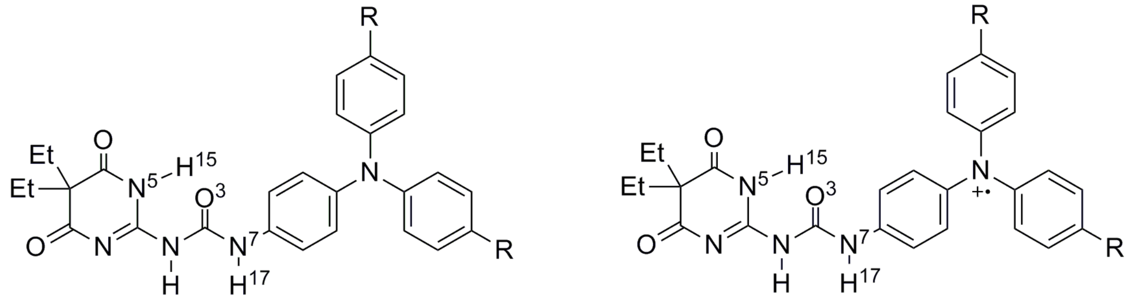
[a] $R1 = \Sigma \,||F_o| - |F_c|| / \Sigma |F_o|$. [b] $wR2 = [\Sigma (w(F_o^2 - F_c^2)^2)/ \Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Representative distances (Å) of hydrogen bonds in crystal structures of **1a** and **1b**.

Compound	N1···O3	N3···N2^1	N4···O2^1
1a	2.567(3)	3.004(3)	2.746(3)
1b	2.599(3)	3.082(3)	2.782(3)

4. DFT calculation

The calculations were performed on simplified models of monomers **1’** and dimer (**1b’**)$_2$ having ethyl substituents instead of butyl groups (Chart S2) as well as on a reference compound **TPB**. The calculations were carried out using the Gaussian09 program package.[S8] The geometries of these compounds were optimised using DFT methods without symmetry constraints. The three-parameterized Becke–Lee–Yang–Parr (B3LYP) hybrid exchange-correlation functional[S9] was used with the 6-31G(d) basis set[S10]; solvent effects were not taken into account. The stability of the optimised gas-phase structure was confirmed by calculating the molecular vibrational frequencies, in which no imaginary frequencies were observed.



1a' (R=OCH$_3$)
1b' (R=H)
1c' (R= CN)

1a'$^{+}$ (R=OCH$_3$)
1b'$^{+}$ (R=H)
1c'$^{+}$ (R= CN)

Chart S2. Structures of model monomers **1’** and one-electron-oxidized species **1’**$^{+}$.

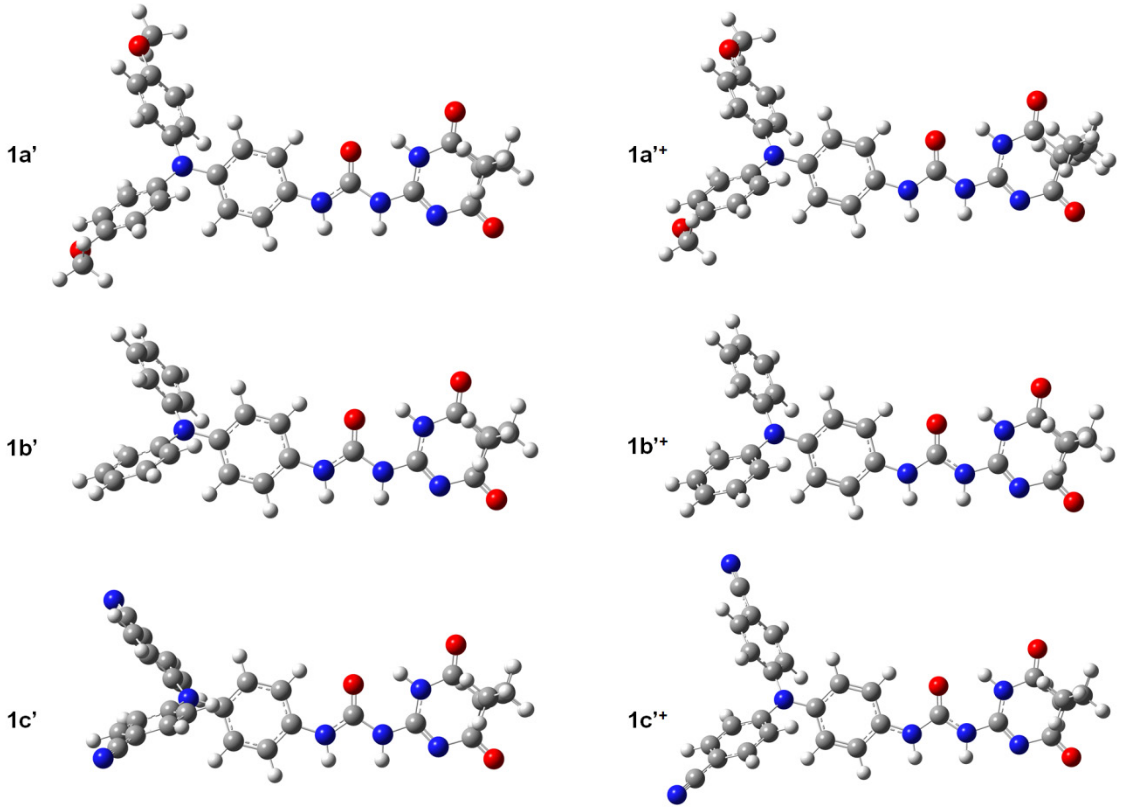


Fig. S11 Optimised structures of model monomers **1'** and **1'**$^{+}$ calculated using a DFT method (B3LYP/6-31G(d) levels of theory).

Table S3. Coordinates of optimised gas-phase geometries of model monomers **1'** and **1'**$^{+}$ calculated using a DFT method (B3LYP/6-31G(d) levels of theory).

Monomer **1a'**

Centre Number	Atomic Number	Coordinates (Å) X	Y	Z
1	8	6.703482	1.878894	1.481303
2	8	8.326734	-1.83513	-1.04108
3	8	2.655386	0.521068	0.506913
4	7	6.096847	-1.46311	-0.84554
5	7	5.342314	0.398019	0.446102
6	7	3.865334	-1.09388	-0.61492
7	7	1.563013	-1.11741	-0.68879
8	6	5.168606	-0.71355	-0.33339
9	6	6.604183	0.89049	0.780199
10	6	7.798065	0.131914	0.208334
11	6	7.429278	-1.13595	-0.60297

12	6	8.575785	1.101372	-0.73445
13	6	8.731109	-0.27618	1.383713
14	6	2.670846	-0.47918	-0.20641
15	1	4.508639	0.879686	0.787567
16	1	3.852507	-1.92499	-1.19451
17	1	1.711349	-1.92771	-1.27526
18	1	8.916768	1.945968	-0.1257
19	1	9.459563	0.555476	-1.07977
20	1	9.617301	-0.73656	0.936462
21	1	9.044439	0.643448	1.888924
22	6	0.197614	-0.78076	-0.49487
23	6	-0.75333	-1.59068	-1.13041
24	6	-0.24361	0.297031	0.284303
25	6	-2.11212	-1.33358	-1.00451
26	1	-0.42922	-2.42761	-1.74706
27	1	0.473753	0.928253	0.789214
28	6	-1.60714	0.539979	0.420805
29	6	-2.56959	-0.26041	-0.21897
30	1	-2.82656	-1.9673	-1.51853
31	1	-1.93215	1.370289	1.038511
32	7	-3.94937	0.003307	-0.0804
33	6	-4.4224	1.342636	0.046814
34	6	-4.89244	-1.06542	-0.06108
35	6	-3.97398	2.351146	-0.81305
36	6	-5.36436	1.675305	1.035687
37	6	-6.06442	-0.99767	-0.83464
38	6	-4.68426	-2.19706	0.735099
39	1	-3.25248	2.110523	-1.58784
40	6	-4.43226	3.66428	-0.68665
41	6	-5.84243	2.972681	1.152142
42	1	-5.72206	0.904535	1.711217
43	1	-6.24169	-0.12624	-1.45723
44	6	-6.99521	-2.02629	-0.80405
45	6	-5.60482	-3.24724	0.752709
46	1	-3.7899	-2.26126	1.347376
47	1	-4.05781	4.420015	-1.36761

48	6	-5.37655	3.98198	0.296294
49	1	-6.57101	3.233534	1.913419
50	1	-7.90256	-1.97649	-1.39795
51	6	-6.77214	-3.16458	-0.01491
52	1	-5.40772	-4.10926	1.379879
53	6	8.107135	-1.23916	2.399086
54	1	7.227516	-0.80298	2.887453
55	1	7.80882	-2.1827	1.9281
56	1	8.830491	-1.47915	3.185883
57	6	7.78271	1.618886	-1.93935
58	1	6.906374	2.20118	-1.63075
59	1	8.411294	2.276009	-2.55002
60	1	7.441608	0.799658	-2.58261
61	8	-5.90062	5.226466	0.50308
62	8	-7.74357	-4.12391	-0.06604
63	6	-7.57331	-5.29142	0.72023
64	1	-6.66921	-5.84488	0.432401
65	1	-7.52333	-5.05438	1.79149
66	1	-8.45085	-5.91201	0.529714
67	6	-5.46445	6.284113	-0.33472
68	1	-4.38278	6.451732	-0.24461
69	1	-5.71233	6.094648	-1.38781
70	1	-5.99615	7.174747	0.00521

Monomer **1b’**

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	8	5.630321	1.90506	1.557051
2	8	7.533642	-1.51634	-1.13734
3	8	1.799204	0.444658	0.505468
4	7	5.291259	-1.33562	-0.94754
5	7	4.39135	0.396094	0.415615
6	7	3.014288	-1.10619	-0.7269
7	7	0.702133	-1.13432	-0.75552
8	6	4.269581	-0.67774	-0.41661
9	6	5.607581	0.9487	0.808045

10	6	6.857778	0.292502	0.242511
11	6	6.563666	-0.91686	-0.65909
12	6	7.752485	-0.16654	1.432777
13	6	7.63386	1.359573	-0.58974
14	6	1.798315	-0.52134	-0.26322
15	1	3.513167	0.805455	0.758227
16	1	2.995554	-1.91986	-1.36294
17	1	0.835701	-1.93359	-1.39154
18	1	8.683765	-0.54885	1.004046
19	1	7.99233	0.728673	2.015682
20	1	7.884405	2.17691	0.094447
21	1	8.569464	0.891903	-0.91192
22	6	-0.65134	-0.78688	-0.51385
23	6	-1.62531	-1.55669	-1.17122
24	6	-1.06465	0.260908	0.322607
25	6	-2.97635	-1.27861	-1.01016
26	1	-1.31583	-2.36606	-1.82499
27	1	-0.33099	0.858314	0.843728
28	6	-2.42226	0.518649	0.492913
29	6	-3.40054	-0.23556	-0.17127
30	1	-3.71284	-1.87449	-1.53941
31	1	-2.72807	1.324688	1.152208
32	7	-4.78181	0.049728	-0.00332
33	6	-5.23084	1.398628	0.020102
34	6	-5.71674	-1.01348	0.122838
35	6	-4.69849	2.345206	-0.87048
36	6	-6.21424	1.806175	0.936457
37	6	-6.95363	-0.95859	-0.54045
38	6	-5.41813	-2.13692	0.911247
39	1	-3.94241	2.038235	-1.58607
40	6	-5.13601	3.667828	-0.83565
41	6	-6.65861	3.126802	0.950709
42	1	-6.62546	1.08324	1.633811
43	1	-7.18946	-0.09729	-1.15722
44	6	-7.87014	-1.99981	-0.40756
45	6	-6.33401	-3.18134	1.023155

46	1	-4.46777	-2.18387	1.433452
47	1	-4.71207	4.386245	-1.53253
48	6	-6.12097	4.067698	0.069924
49	1	-7.42027	3.42353	1.667188
50	1	-8.82231	-1.93957	-0.92841
51	6	-7.56671	-3.11955	0.369868
52	1	-6.08578	-4.04224	1.638613
53	1	-6.46412	5.098136	0.089424
54	1	-8.28095	-3.93237	0.465584
55	6	7.125485	-1.226	2.344827
56	1	7.821324	-1.48987	3.148192
57	1	6.204998	-0.86369	2.817089
58	1	6.892461	-2.14705	1.798027
59	6	6.881895	1.912891	-1.8047
60	1	5.957119	2.42471	-1.51409
61	1	7.505607	2.642749	-2.33147
62	1	6.626441	1.123201	-2.52083

Monomer **1c’**

Centre	Atomic	Coordinates (Å)		
Number	Number	X	Y	Z
1	8	6.267445	1.361235	2.06612
2	8	8.221019	-1.16768	-1.45168
3	8	2.454412	0.367845	0.502511
4	7	5.976214	-1.01554	-1.27193
5	7	5.050858	0.26956	0.503552
6	7	3.695577	-0.82728	-1.05377
7	7	1.384487	-0.85753	-1.12221
8	6	4.94556	-0.52033	-0.60145
9	6	6.261205	0.649289	1.082846
10	6	7.520862	0.116055	0.41845
11	6	7.243544	-0.72947	-0.83365
12	6	8.28309	-0.76525	1.457111
13	6	8.419551	1.327951	0.028533
14	6	2.473502	-0.37888	-0.47838
15	1	4.170137	0.598472	0.916079

16	1	3.689621	-1.4396	-1.88603
17	1	1.530118	-1.4943	-1.92024
18	1	9.226157	-1.06359	0.988541
19	1	8.520906	-0.11912	2.308393
20	1	8.643822	1.86893	0.953397
21	1	9.358217	0.919832	-0.35803
22	6	0.030177	-0.59592	-0.80907
23	6	-0.9336	-1.23105	-1.61204
24	6	-0.39342	0.245428	0.232074
25	6	-2.28836	-1.02419	-1.38561
26	1	-0.61245	-1.87761	-2.42229
27	1	0.334415	0.734728	0.862169
28	6	-1.7547	0.431397	0.460215
29	6	-2.71612	-0.19275	-0.34218
30	1	-3.02221	-1.5116	-2.02006
31	1	-2.07386	1.073838	1.275273
32	7	-4.11239	0.014201	-0.1022
33	6	-4.61078	1.334538	-0.0226
34	6	-4.96015	-1.10654	0.046349
35	6	-4.07025	2.347155	-0.83659
36	6	-5.63568	1.667694	0.883127
37	6	-6.27548	-1.092	-0.45578
38	6	-4.49034	-2.27149	0.681094
39	1	-3.28121	2.104294	-1.53966
40	6	-4.54083	3.649805	-0.75057
41	6	-6.11425	2.967958	0.961265
42	1	-6.04907	0.903546	1.532385
43	1	-6.64758	-0.20948	-0.96469
44	6	-7.09713	-2.20161	-0.31664
45	6	-5.30824	-3.38504	0.810349
46	1	-3.48089	-2.29471	1.076559
47	1	-4.12036	4.420731	-1.3883
48	6	-5.57231	3.97733	0.146465
49	1	-6.90059	3.213739	1.667756
50	1	-8.10697	-2.18049	-0.71373
51	6	-6.62403	-3.36451	0.316133

52	1	-4.93662	-4.27509	1.307936
53	6	7.525849	-2.00553	1.942957
54	1	8.140861	-2.56445	2.655845
55	1	6.59409	-1.7403	2.455834
56	1	7.281969	-2.68493	1.117825
57	6	7.805438	2.286501	-0.99683
58	1	6.87928	2.740459	-0.62585
59	1	8.502816	3.102322	-1.21366
60	1	7.586286	1.782215	-1.94523
61	6	-7.4682	-4.5122	0.451938
62	7	-8.15354	-5.44663	0.561648
63	6	-6.06173	5.319626	0.230786
64	7	-6.45963	6.411378	0.298374

Monomer **1a’**$^{+}$

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	8	6.662149	1.843553	1.515877
2	8	8.259832	-1.84126	-1.06923
3	8	2.56898	0.465032	0.530767
4	7	6.034062	-1.45715	-0.85747
5	7	5.294304	0.379503	0.469411
6	7	3.804477	-1.10111	-0.61976
7	7	1.500111	-1.14897	-0.72382
8	6	5.12039	-0.71565	-0.32666
9	6	6.567696	0.867214	0.801821
10	6	7.755393	0.116085	0.210433
11	6	7.379313	-1.13824	-0.61447
12	6	8.527851	1.098693	-0.726
13	6	8.697431	-0.31002	1.374289
14	6	2.6251	-0.51026	-0.20628
15	1	4.477969	0.864867	0.836614
16	1	3.806273	-1.92394	-1.21282
17	1	1.656633	-1.92368	-1.35619
18	1	8.872431	1.934068	-0.10724
19	1	9.410134	0.557426	-1.08158

20	1	9.578508	-0.7662	0.913388
21	1	9.01816	0.603096	1.88599
22	6	0.161214	-0.81549	-0.51866
23	6	-0.80486	-1.55315	-1.23576
24	6	-0.26851	0.200402	0.360635
25	6	-2.15437	-1.28947	-1.09078
26	1	-0.48825	-2.32874	-1.92865
27	1	0.459356	0.760522	0.928955
28	6	-1.62134	0.464663	0.499593
29	6	-2.58424	-0.26857	-0.2201
30	1	-2.87941	-1.84832	-1.67216
31	1	-1.94153	1.231929	1.196319
32	7	-3.96157	0.016436	-0.07378
33	6	-4.39692	1.353525	0.036891
34	6	-4.90018	-1.03765	-0.03977
35	6	-3.78481	2.369594	-0.72413
36	6	-5.45473	1.691062	0.913522
37	6	-6.14909	-0.90352	-0.6893
38	6	-4.60519	-2.23395	0.642799
39	1	-2.99227	2.116309	-1.41998
40	6	-4.20992	3.685196	-0.62123
41	6	-5.87579	2.999096	1.022015
42	1	-5.91413	0.92171	1.524436
43	1	-6.37498	0.003276	-1.23983
44	6	-7.06291	-1.93544	-0.65624
45	6	-5.52488	-3.27146	0.682907
46	1	-3.66197	-2.33307	1.169382
47	1	-3.73627	4.444101	-1.23202
48	6	-5.26237	4.016004	0.255837
49	1	-6.67032	3.27792	1.705786
50	1	-8.01652	-1.85715	-1.16722
51	6	-6.76664	-3.13373	0.031353
52	1	-5.28304	-4.17269	1.233087
53	6	8.079389	-1.28289	2.383534
54	1	7.205343	-0.8504	2.88542
55	1	7.776767	-2.22217	1.90646

56	1	8.809263	-1.53167	3.160808
57	6	7.729003	1.631574	-1.92006
58	1	6.853357	2.209638	-1.60068
59	1	8.35504	2.298059	-2.52229
60	1	7.388264	0.821948	-2.57586
61	8	-5.75106	5.250083	0.435735
62	8	-7.7258	-4.06913	0.002554
63	6	-7.51418	-5.32425	0.659221
64	1	-6.65213	-5.84823	0.232091
65	1	-7.37409	-5.18305	1.736539
66	1	-8.42063	-5.90145	0.480011
67	6	-5.18488	6.35084	-0.28563
68	1	-4.12504	6.475684	-0.03852
69	1	-5.30742	6.213779	-1.36554
70	1	-5.74382	7.227843	0.038861

Monomer **1b’**$^{+}$

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	8	5.841035	2.148268	1.226453
2	8	7.417936	-1.8	-0.95423
3	8	1.727604	0.698014	0.357788
4	7	5.19458	-1.39706	-0.75574
5	7	4.465069	0.592758	0.334059
6	7	2.967882	-0.99944	-0.58104
7	7	0.662646	-1.08359	-0.65527
8	6	4.287393	-0.58808	-0.32487
9	6	5.74318	1.088935	0.64465
10	6	6.926444	0.225905	0.219997
11	6	6.543764	-1.06418	-0.54316
12	6	7.711563	-0.1814	1.50647
13	6	7.859446	1.083799	-0.68617
14	6	1.793165	-0.36625	-0.23924
15	1	3.654385	1.139649	0.61598
16	1	2.971872	-1.88729	-1.07216
17	1	0.823258	-1.94658	-1.16064

18	1	8.594784	-0.7327	1.16949
19	1	8.053454	0.742701	1.98406
20	1	8.190859	1.942487	-0.09334
21	1	8.735769	0.466094	-0.9042
22	6	-0.66973	-0.75056	-0.46812
23	6	-1.63841	-1.62217	-1.02277
24	6	-1.1047	0.393621	0.242524
25	6	-2.98545	-1.37361	-0.87637
26	1	-1.31853	-2.49253	-1.58987
27	1	-0.37575	1.054336	0.688215
28	6	-2.45517	0.646772	0.378225
29	6	-3.42484	-0.22557	-0.17218
30	1	-3.70907	-2.03787	-1.33442
31	1	-2.77573	1.509771	0.950651
32	7	-4.78876	0.038027	-0.02357
33	6	-5.26532	1.376786	0.021906
34	6	-5.72092	-1.0312	0.086844
35	6	-4.74514	2.339305	-0.86424
36	6	-6.26619	1.729056	0.946702
37	6	-6.94255	-0.96553	-0.60825
38	6	-5.42239	-2.14161	0.898493
39	1	-4.00007	2.052771	-1.59895
40	6	-5.22437	3.643562	-0.81616
41	6	-6.73014	3.038697	0.986015
42	1	-6.64806	0.986634	1.639092
43	1	-7.15655	-0.11486	-1.24639
44	6	-7.85032	-2.01236	-0.49473
45	6	-6.344	-3.17743	1.006688
46	1	-4.49437	-2.1674	1.459997
47	1	-4.83596	4.382421	-1.50995
48	6	-6.21362	3.998043	0.107543
49	1	-7.48969	3.3156	1.710237
50	1	-8.78627	-1.97077	-1.04282
51	6	-7.5563	-3.11815	0.311009
52	1	-6.1233	-4.02593	1.646645
53	1	-6.58317	5.018196	0.141035

54	1	-8.27181	-3.92976	0.399159
55	6	6.923467	-1.02683	2.512314
56	1	7.553323	-1.26711	3.37496
57	1	6.042788	-0.49473	2.892014
58	1	6.592778	-1.97617	2.07508
59	6	7.226411	1.566513	-1.99506
60	1	6.361643	2.216965	-1.81581
61	1	7.95363	2.146863	-2.57209
62	1	6.905535	0.727633	-2.62352

Monomer **1c’**$^+$

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	8	6.548075	2.071343	1.248222
2	8	8.115409	-1.881616	-0.932019
3	8	2.422577	0.636941	0.347843
4	7	5.893749	-1.465134	-0.745743
5	7	5.168746	0.52569	0.344221
6	7	3.668527	-1.059142	-0.585662
7	7	1.362898	-1.141135	-0.680711
8	6	4.990009	-0.651944	-0.318232
9	6	6.449725	1.014588	0.663099
10	6	7.630616	0.147022	0.241629
11	6	7.245418	-1.139927	-0.524445
12	6	8.409811	-0.265199	1.530513
13	6	8.570227	1.002393	-0.660815
14	6	2.496724	-0.424395	-0.25115
15	1	4.361903	1.078574	0.624101
16	1	3.675383	-1.946163	-1.078864
17	1	1.526766	-2.002667	-1.188561
18	1	9.291946	-0.819479	1.195711
19	1	8.753895	0.657025	2.010015
20	1	8.902949	1.85882	-0.065554
21	1	9.444921	0.381471	-0.876152
22	6	0.03534	-0.807046	-0.501638
23	6	-0.934641	-1.675942	-1.06533

24	6	-0.40257	0.338576	0.210666
25	6	-2.280063	-1.424033	-0.926505
26	1	-0.613612	-2.544684	-1.634019
27	1	0.325698	0.994825	0.66419
28	6	-1.751438	0.594517	0.338026
29	6	-2.721479	-0.274968	-0.221152
30	1	-3.001625	-2.084736	-1.392998
31	1	-2.072103	1.456015	0.912764
32	7	-4.08373	-0.008452	-0.080175
33	6	-4.558226	1.331439	-0.021335
34	6	-5.022754	-1.074474	0.009818
35	6	-4.038394	2.300859	-0.899323
36	6	-5.557374	1.677938	0.906768
37	6	-6.234383	-1.000009	-0.700946
38	6	-4.741014	-2.19111	0.81819
39	1	-3.293684	2.023169	-1.637427
40	6	-4.510273	3.60426	-0.84482
41	6	-6.022826	2.983146	0.96273
42	1	-5.943399	0.933115	1.594028
43	1	-6.440827	-0.145575	-1.336265
44	6	-7.149688	-2.03848	-0.611997
45	6	-5.661338	-3.225428	0.910047
46	1	-3.821863	-2.227779	1.393055
47	1	-4.126436	4.352398	-1.529867
48	6	-5.503796	3.956449	0.087679
49	1	-6.780452	3.261093	1.68735
50	1	-8.078554	-1.99588	-1.170335
51	6	-6.870763	-3.158792	0.193692
52	1	-5.459234	-4.080991	1.545298
53	6	7.614752	-1.108476	2.532591
54	1	8.240758	-1.352114	3.396996
55	1	6.73511	-0.573138	2.910198
56	1	7.281914	-2.056298	2.093574
57	6	7.94366	1.489145	-1.971298
58	1	7.080716	2.142732	-1.794511
59	1	8.675197	2.067674	-2.54452

60	1	7.622379	0.652504	-2.602599
61	6	-7.817378	-4.228659	0.286524
62	7	-8.584501	-5.099464	0.360954
63	6	-5.988589	5.302056	0.143628
64	7	-6.381688	6.395594	0.188877

Table S4. Mulliken values for key atoms involved in hydrogen-bond formations of model monomers **1’**.

	1a’	**1b’**	**1c’**	*Δ*[a]
O3	-0.53855	-0.53637	-0.53202	0.00653
N7	-0.75943	-0.76015	-0.76341	0.00398
H17	0.334469	0.335587	0.338962	0.004493
H17[b]	0.350225[b]	0.356001[b]	0.360277[b]	0.008027

[a] The differences between the maximum and the minimum values in the series. [b] The values for the one-electron-oxidized species **1’**$^{+}$.

Table S5. Representative N5···O3 distances (Å) of intramolecular hydrogen-bonds in the DFT-optimized structures of **1’** and **1’**$^{+}$.

1a’	2.69043	**1a’**$^{+}$	2.72736
1b’	2.69211	**1b’**$^{+}$	2.73959
1c’	2.70031	**1c’**$^{+}$	2.74842

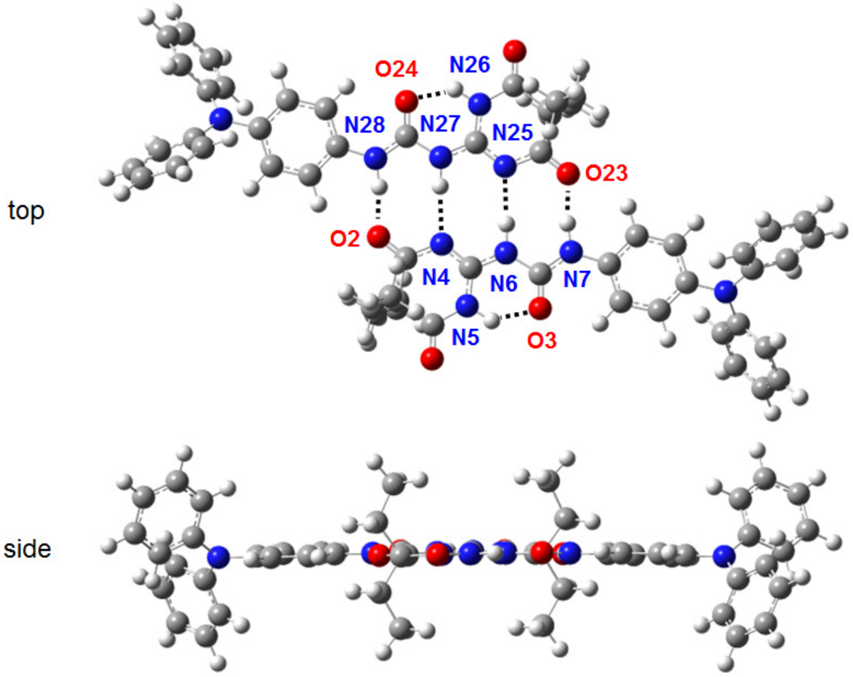


Fig. S12 Top and side views of optimised structure of (**1b'**)$_2$ calculated using a DFT method (B3LYP/6-31G(d) levels of theory). Selected N···O and N···N distances (Å): N4···N27 3.09314, N5···O3 2.59412, N6···N25 3.09313, N7···O23 2.79690, N28···O2 2.79690, N26···O24 2.59416.

Table S6. Coordinates of optimised gas-phase geometry of (**1b'**)$_2$ calculated using a DFT method (B3LYP/6-31G(d) levels of theory).

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	8	0.262839	5.668151	-0.10419
2	8	-2.86438	2.089826	-0.03721
3	8	3.373857	2.79829	-0.13891
4	7	-0.64814	1.660784	-0.07163
5	7	0.874074	3.490699	-0.10524
6	7	1.618369	1.276093	-0.10096
7	7	3.811055	0.541509	-0.0877
8	6	0.580761	2.158648	-0.0926
9	6	-0.08155	4.503139	-0.08696
10	6	-1.53435	4.055462	-0.03818
11	6	-1.70841	2.528547	-0.05179

12	6	-2.17431	4.619994	1.267708
13	6	-2.27662	4.662603	-1.26634
14	6	3.002718	1.621189	-0.11197
15	1	1.872195	3.734491	-0.12724
16	1	1.325007	0.285788	-0.08729
17	1	3.375899	-0.39196	-0.06584
18	1	-2.0922	5.710692	1.217171
19	1	-3.23728	4.361	1.237962
20	1	-3.33486	4.405714	-1.15958
21	1	-2.1845	5.750839	-1.18909
22	8	-0.26283	-5.66816	-0.1042
23	8	2.864376	-2.08982	-0.03724
24	8	-3.37388	-2.79828	-0.13898
25	7	0.648137	-1.66079	-0.07164
26	7	-0.87407	-3.49071	-0.10526
27	7	-1.61837	-1.2761	-0.10097
28	7	-3.81106	-0.5415	-0.08774
29	6	-0.58076	-2.15865	-0.09261
30	6	0.081563	-4.50314	-0.08698
31	6	1.534359	-4.05546	-0.03819
32	6	1.70841	-2.52855	-0.05181
33	6	2.27664	-4.66261	-1.26633
34	6	2.174308	-4.61998	1.267711
35	6	-3.00273	-1.62119	-0.11201
36	1	-1.87219	-3.7345	-0.12727
37	1	-1.32501	-0.28579	-0.08729
38	1	-3.3759	0.391969	-0.06585
39	1	3.334873	-4.40572	-1.15957
40	1	2.184527	-5.75085	-1.18907
41	1	2.092204	-5.71068	1.217183
42	1	3.237278	-4.36098	1.237974
43	6	5.228971	0.536858	-0.06528
44	6	5.852922	-0.72028	-0.00495
45	6	6.027069	1.690324	-0.09532
46	6	7.237108	-0.82335	0.039617
47	1	5.244344	-1.61864	0.024361

48	1	5.566036	2.665561	-0.15079
49	6	7.414385	1.575158	-0.07039
50	6	8.044902	0.324637	0.004813
51	1	7.6997	-1.80297	0.102494
52	1	8.019694	2.475278	-0.10614
53	7	9.460896	0.221914	0.048361
54	6	10.21437	1.124608	0.847819
55	6	10.1227	-0.79462	-0.69266
56	6	9.767337	1.490552	2.127972
57	6	11.41847	1.666077	0.36842
58	6	11.19248	-1.50804	-0.12746
59	6	9.716437	-1.10339	-2.00128
60	1	8.841044	1.072713	2.509209
61	6	10.50569	2.383339	2.902399
62	6	12.15908	2.543416	1.158042
63	1	11.76749	1.395099	-0.62294
64	1	11.50825	-1.28049	0.885643
65	6	11.8432	-2.49843	-0.86059
66	6	10.36191	-2.10812	-2.71965
67	1	8.895659	-0.55162	-2.44845
68	1	10.14356	2.654987	3.890608
69	6	11.70746	2.912288	2.426941
70	1	13.08842	2.952308	0.769913
71	1	12.66912	-3.03987	-0.40646
72	6	11.43119	-2.80927	-2.15825
73	1	10.03418	-2.33238	-3.73151
74	1	12.28347	3.602752	3.036374
75	1	11.93652	-3.58667	-2.72418
76	6	-5.22897	-0.53685	-0.06536
77	6	-5.85293	0.720293	-0.00505
78	6	-6.02707	-1.69032	-0.09542
79	6	-7.23711	0.823353	0.039481
80	1	-5.24435	1.618648	0.024276
81	1	-5.56603	-2.66555	-0.15088
82	6	-7.41438	-1.57515	-0.07053
83	6	-8.04491	-0.32463	0.004659

84	1	-7.69971	1.802975	0.102343
85	1	-8.01969	-2.47527	-0.10629
86	7	-9.4609	-0.22191	0.048172
87	6	-10.2144	-1.1246	0.847628
88	6	-10.1227	0.794603	-0.69289
89	6	-9.76738	-1.49052	2.127794
90	6	-11.4185	-1.66607	0.368215
91	6	-11.1925	1.508022	-0.12774
92	6	-9.71638	1.103359	-2.0015
93	1	-8.84109	-1.07268	2.509042
94	6	-10.5057	-2.3833	2.90222
95	6	-12.1591	-2.5434	1.157836
96	1	-11.7675	-1.39511	-0.62316
97	1	-11.5083	1.280489	0.885357
98	6	-11.8432	2.498394	-0.86091
99	6	-10.3618	2.108072	-2.71991
100	1	-8.89558	0.55159	-2.44863
101	1	-10.1436	-2.65493	3.890439
102	6	-11.7075	-2.91226	2.426748
103	1	-13.0884	-2.9523	0.769696
104	1	-12.6691	3.039834	-0.40681
105	6	-11.4311	2.809219	-2.15856
106	1	-10.0341	2.332319	-3.73176
107	1	-12.2835	-3.60271	3.03618
108	1	-11.9365	3.586607	-2.72452
109	6	1.762276	-4.1948	-2.63162
110	1	2.340023	-4.66722	-3.43302
111	1	0.711042	-4.46487	-2.78516
112	1	1.860365	-3.10982	-2.75328
113	6	-1.76225	4.194776	-2.63162
114	1	-2.33999	4.667183	-3.43303
115	1	-0.71102	4.464835	-2.78516
116	1	-1.86034	3.109791	-2.75326
117	6	1.550265	-4.1132	2.572126
118	1	0.492951	-4.3908	2.653684
119	1	2.068693	-4.5518	3.431228

120	1	1.627016	-3.02361	2.664836
121	6	-1.55028	4.113226	2.572133
122	1	-0.49297	4.390813	2.653698
123	1	-2.06872	4.551833	3.431226
124	1	-1.62704	3.02363	2.66485

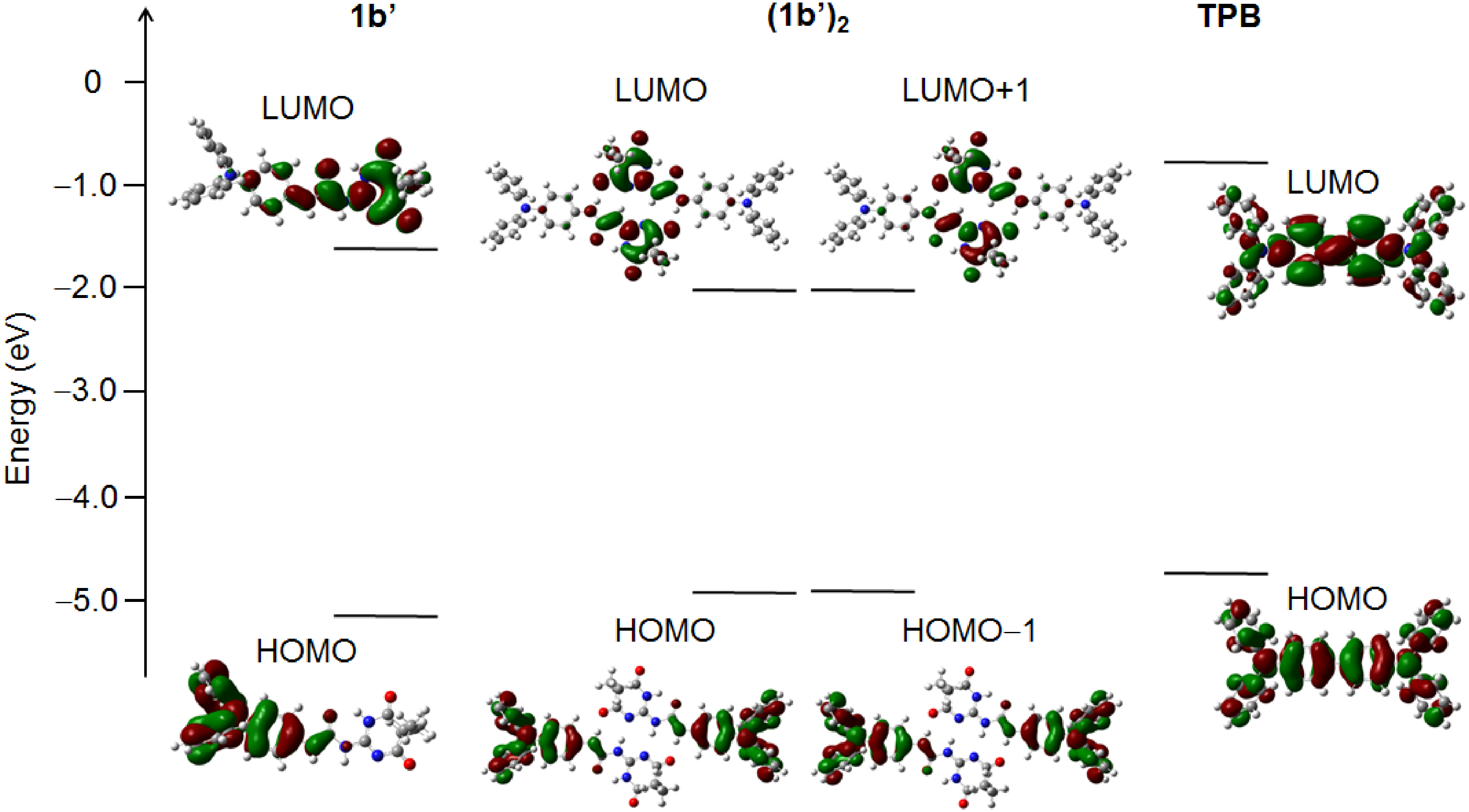


Fig. S13 Selected molecular orbital contributions and energy diagrams for **1b’**, **(1b’)$_2$** and TPD calculated using a DFT method (B3LYP/6-31G(d) levels of theory). The difference in HOMO levels between **1b’** and (**1b’**)$_2$ is 0.24 eV in gas phase.

5. The method for calculating K_{dim}

The ^{1}H-NMR data was fitted to a dimerization isotherm by solving the following equations.[S11]

$$A + A \overset{K_{dim}}{\longleftrightarrow} AA$$

$$K_{dim} = \frac{[AA]}{[A]^2}$$

$$[A] = [A]_0 - 2[AA]$$

$$\delta_{obs} = \frac{2[AA]}{[A]_0}\delta_d + \frac{[A]}{[A]_0}\delta_f$$

Where

[A]$_0$ is the total concentration

[A] is the concentration of unbound free species

[AA] is the concentration of dimer

K_{dim} is the dimerization constant

δ_{f} is the free chemical shift of the monomer

δ_{d} is the limiting bound chemical shift of the dimer

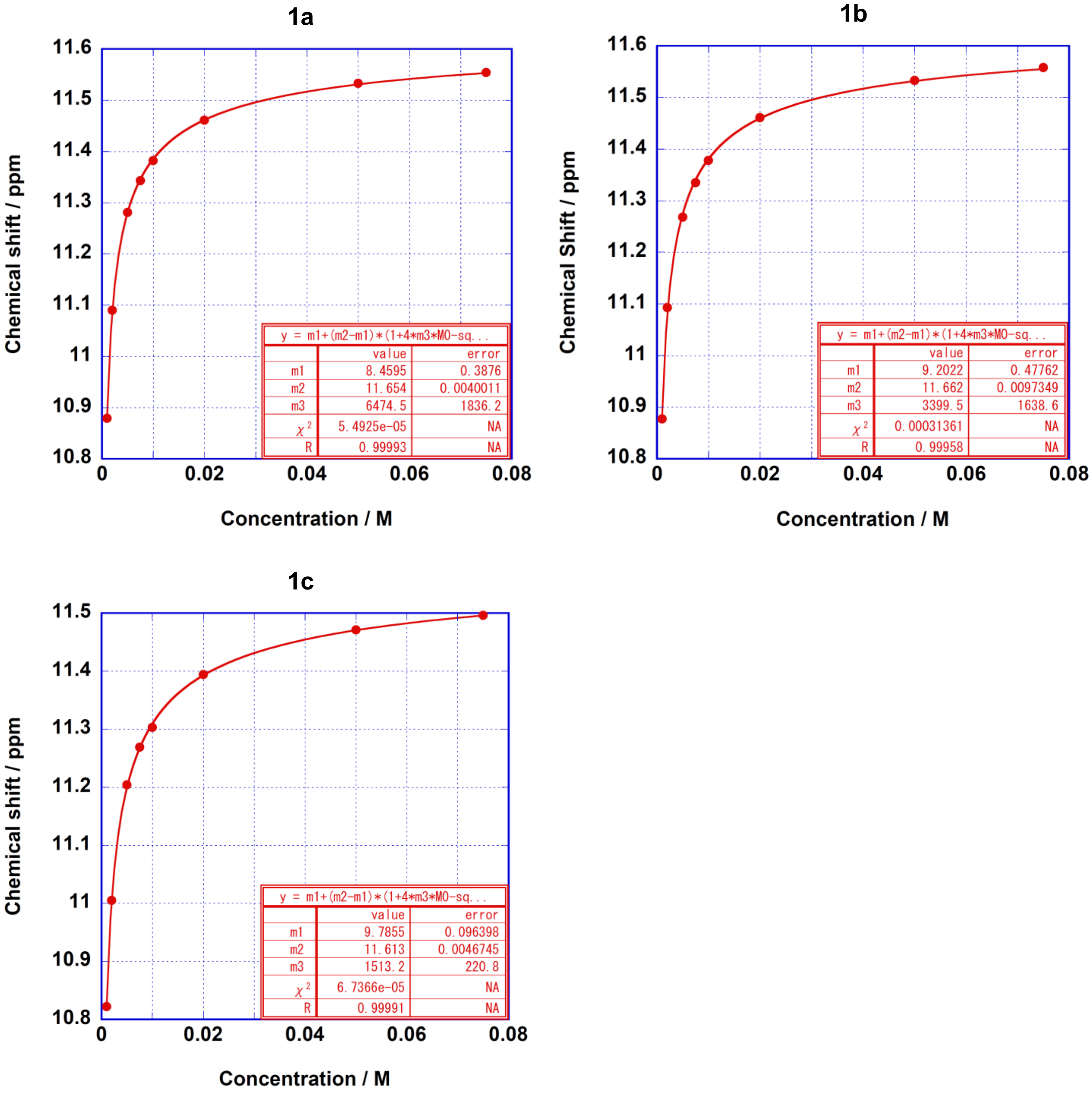
δ_{obs} is the observed chemical shift

From these equations above, the dimerization equation can be obtained to fit δ_{obs} *vs.* [A]$_0$.

$$[AA] = \frac{1 + 4K_{dim}[A]_0 - \sqrt{1 + 8K_{dim}[A]_0}}{8K_{dim}}$$

$$\delta_{obs} = \delta_f + (\delta_d - \delta_f)\frac{1 + 4K_{dim}[A]_0 - \sqrt{1 + 8K_{dim}[A]_0}}{4K_{dim}[A]_0}$$

The chemical shifts at each concentration were recorded and fitted into a dimerization equation to determine K_{dim}, δ_{f} and δ_{d}.



1a: y = m1+(m2-m1)*(1+4*m3*M0-sq...

	value	error
m1	8.4595	0.3876
m2	11.654	0.0040011
m3	6474.5	1836.2
χ^2	5.4925e-05	NA
R	0.99993	NA

1b: y = m1+(m2-m1)*(1+4*m3*M0-sq...

	value	error
m1	9.2022	0.47762
m2	11.662	0.0097349
m3	3399.5	1638.6
χ^2	0.00031361	NA
R	0.99958	NA

1c: y = m1+(m2-m1)*(1+4*m3*M0-sq...

	value	error
m1	9.7855	0.096398
m2	11.613	0.0046745
m3	1513.2	220.8
χ^2	6.7366e-05	NA
R	0.99991	NA

Fig. S14 Determination of the dimerization constants (K_{dim}) of **1** between 1.0 and 75 mM in $CDCl_3$ at 293 K. The fitting results are based on the middle field NH protons among three NH protons. Fitting based on the highest field NH protons gave similar K_{dim} values.

6. Electrochemical and spectroelectrochemical measurements

All voltammetric experiments were carried out using a BAS electrochemical analyzer (Bioanalytical Systems Inc, West Lafayette, IN, USA). All experiments were performed using a conventional three-electrode system at room temperature. A platinum wire (1.6 mm in diameter) was employed as the counter electrode, a glassy carbon electrode (3.0 mm in diameter) as the working electrode and an Ag/AgCl (3.0 M NaCl) electrode as the reference electrode. Nonaqueous CH_2Cl_2 solutions containing **1** and *n*-Bu_4NPF_6 (0.1 M) were deaerated prior to each measurement, and an argon atmosphere was maintained inside the cell throughout each measurement. Reference compounds (**TPB** and TPA derivatives) were also measured under similar conditions (Table S6). Each experiment was first performed in the absence of any internal standard and then repeated in the presence of decamethylferrocene (Fc*). A separate experiment containing only ferrocene and decamethylferrocene was also performed. The potentials are quoted relative to Fc^{*+}/Fc^* couple. In this setup, the Fc^+/Fc couple was observed at 560 and 536 mV *vs.* Fc^{*+}/Fc^* while the Fc^+/Fc couple was at 664 and 562 mV *vs.* Ag/AgCl in CH_2Cl_2/*n*-Bu_4NPF_6 and 1,2-dichloroethane/*n*-Bu_4NPF_6, respectively. The potential data quoted relative to the Fc^+/Fc couple are also shown in Tables S7.

The controlled-potential electrolysis of **1a** was followed by UV-vis-NIR measurements using an optical thin-layer quartz cell (0.1 cm). The working and counter electrodes made from a platinum mesh and a platinum wire, respectively, were used along with an Ag/AgCl reference electrode. The applied potential between the working and reference electrodes was maintained constant with a bulk electrolysis technique of the BAS analyzer.

Table S7. Electrochemical data for TPA derivatives in CH_2Cl_2/*n*-Bu_4NPF_6.[a]

Compound	$E_{ox}^{1\,b}$
TPAa	849
TPAb	1154
TPAc	1571

[a] Potentials in mV vs. Fc^{*+}/Fc^* (Fc = decamethylferrocene). [b] ΔE_{ox}^1 (not reversible).

Table S8. Electrochemical data for **1** and reference compounds in $CH_2Cl_2/n\text{-}Bu_4NPF_6$.[a]

Compound	$E_{1/2}{}^1$	$E_{1/2}{}^2$	$\Delta E_{1/2}{}^b$	$K_c{}^c$
1a	145	810	665	1.75×10^{11}
1a[d]	159	818	659	1.38×10^{11}
1b	391	832	441	2.85×10^{7}
1c	753	891	138	211
TPB	272	523	251	1.75×10^{4}
TPAa	289[e]	–	–	–
TPAb	594[e]	–	–	–
TPAc	1011[e]	–	–	–

[a] Potentials in mV vs. Fc^+/Fc (Fc = ferrocene). [b] $\Delta E_{1/2}$ = potential difference between two redox processes. [c] Comproportionation constants obtained from $K_c = \exp(\Delta E_{1/2} F/RT)$. [d] In 1,2-dichloroethane. [e] $E_{ox}{}^1$ potentials (not reversible).

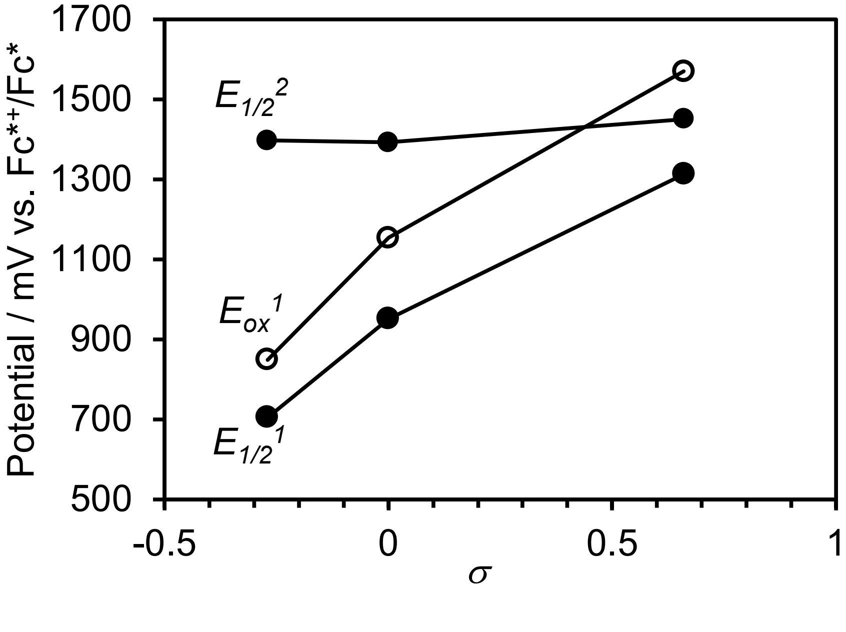


Fig. S15 Plot of $E_{1/2}{}^1$ and $E_{1/2}{}^2$ potentials of $(\mathbf{1})_2$ (filled circles) and $E_{ox}{}^1$ potentials of reference compounds (**TPAa**, **TPAb** and **TPAc**) (circles) in $CH_2Cl_2/n\text{-}Bu_4NPF_6$ against the Hammett para parameter .

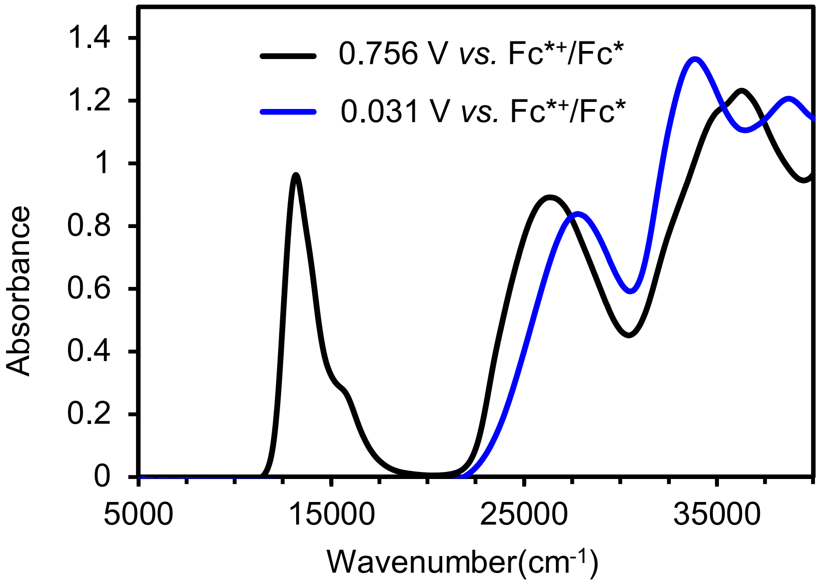


Fig. S16 UV-vis-NIR spectra of a CH_2Cl_2 solution containing **1a** (5.0 x 10^{-4} M) and *n*-Bu_4NPF_6 (0.10 M) before and after the controlled potential electrolysis (at 0.031 V and 0.756 V ($E_{ox}^{1} = E_{1/2}^{1} + 0.051$ mV) *vs*. Fc^{*+}/Fc^{*}).

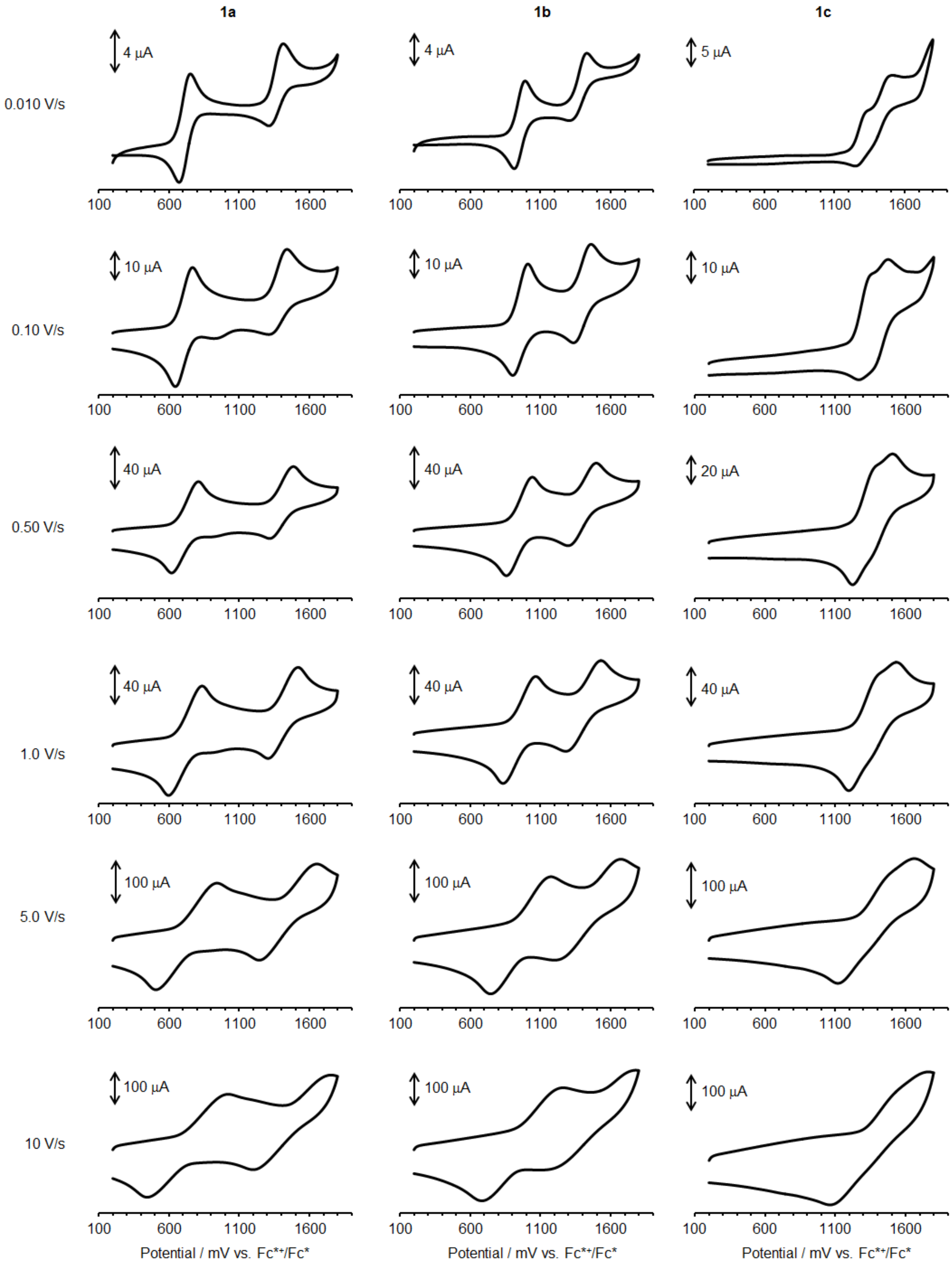


Fig. S17 Cyclic voltammograms of **1** (1.0 mM) in CH_2Cl_2 containing *n*-Bu_4NPF_6 (0.1 M) at various scan rates.

7. Chemical oxidation

Chemical oxidation of **1a** was performed with $SbCl_5$ in a homogeneous CH_2Cl_2 solution. The reaction was followed by UV-vis-NIR measurements using an optical thin-layer quartz cell (0.1 cm) as shown in Fig. S18. We chose $SbCl_5$ because it has been used for chemical oxidation of triphenylamine derivatives as a homogeneous oxidizing agent.[S12a] Electron transfer occurs according to eq. S1 although complications can come from the antimony-containing reaction product, which may itself be an oxidant as expressed by eq. S2.[S12b]

$$3SbCl_5 + 2e^- \rightleftharpoons 2[SbCl_6]^- + SbCl_3 \qquad \text{(S1)}$$

$$[SbCl_6]^- + 2e^- \rightleftharpoons [SbCl_4]^- + 2Cl^- \qquad \text{(S2)}$$

Thus, chemical oxidation of **1a** and **1b** was also performed with $AgSbF_6$ as a heterogeneous oxidizing agent in CH_2Cl_2 followed by filtration of the reaction mixture and the UV-Vis-NIR absorption measurements for the filtrate (Figs. 4 and S19). Chemical oxidation of **1a** was also performed with $AgSbF_6$ in 1,2-dichlorethane (Fig. S20). Chemical oxidation of **1b** (210 mg, 0.400 mol) was furthermore performed with $Cu(ClO_4)_2$ (222 mg, 0.600 mol) in 50mL of CH_2Cl_2 and 30 mL of CH_3CN. After 19 h of stirring at room temperature, the homogeneous reaction solution was analyzed by the MALDI-TOF-MS measurement (Fig. S22).

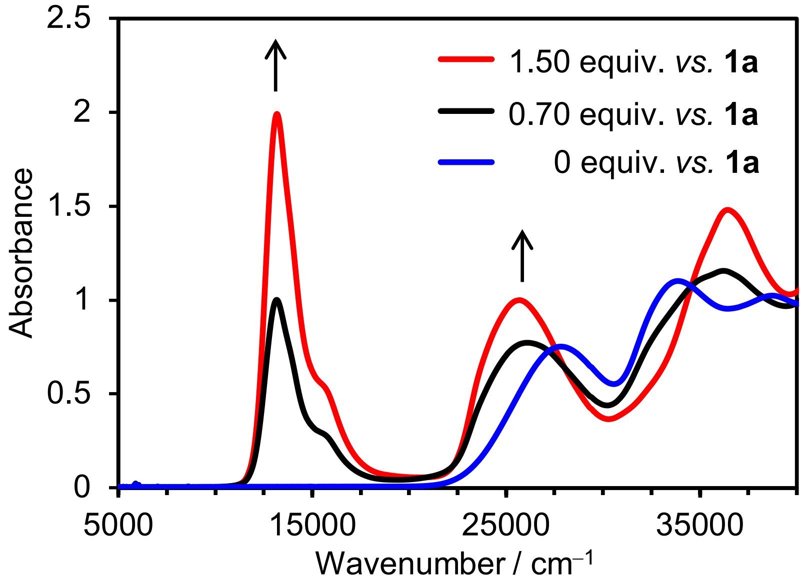


Fig. S18 UV-vis-NIR spectra of **1a** (5.0×10^{-4} M) in the absence and presence of $SbCl_5$ at 298K in CH_2Cl_2.

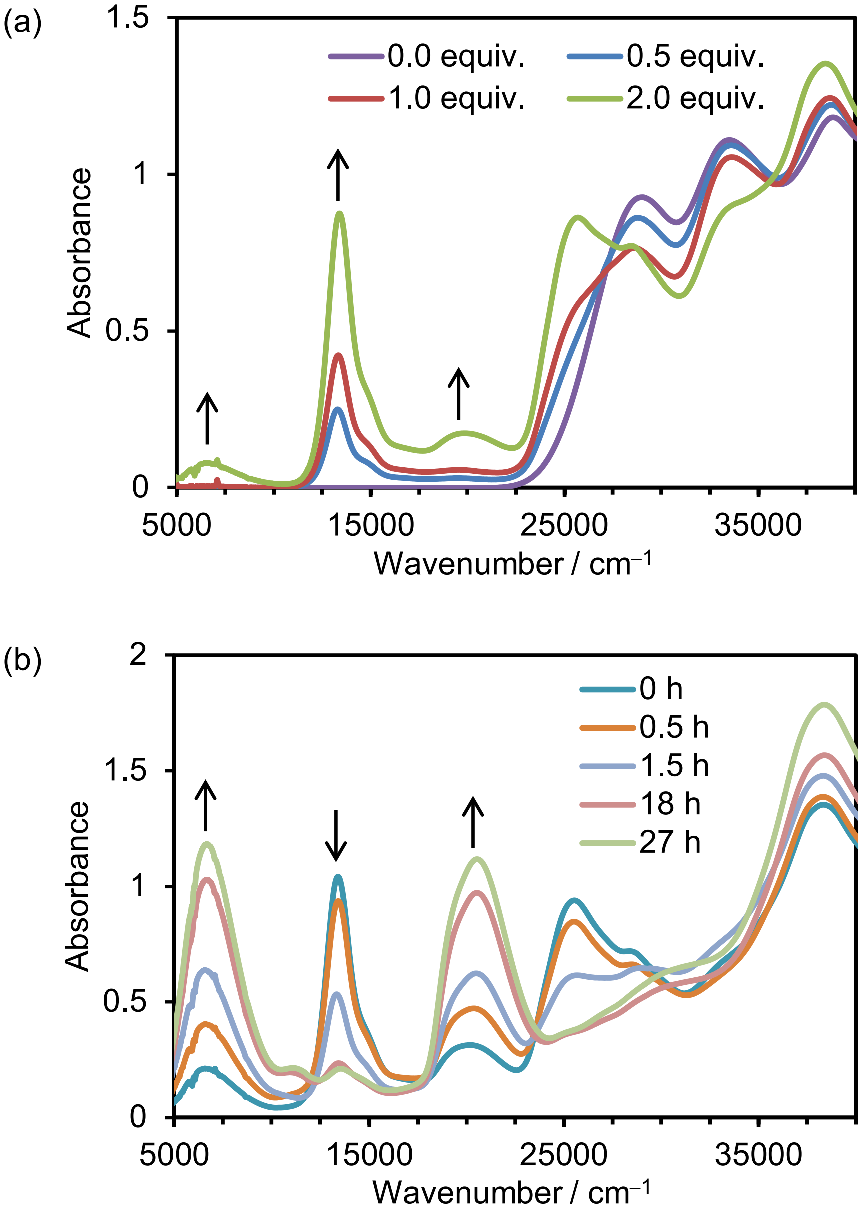


Fig. S19 (a) UV-vis-NIR spectra of **1b** (5.0×10^{-4} M) with 0 to 2.0 equiv. of $AgSbF_6$ *vs.* **1b** in CH_2Cl_2 at 298K. Every spectrum was recorded 15 min after the addition of $AgSbF_6$. (b) Time-dependent change in the absorption spectra of **1b** (5.0×10^{-4} M) in the presence of 4.0 equiv. of $AgSbF_6$ *vs.* **1b** in CH_2Cl_2 at 298K.

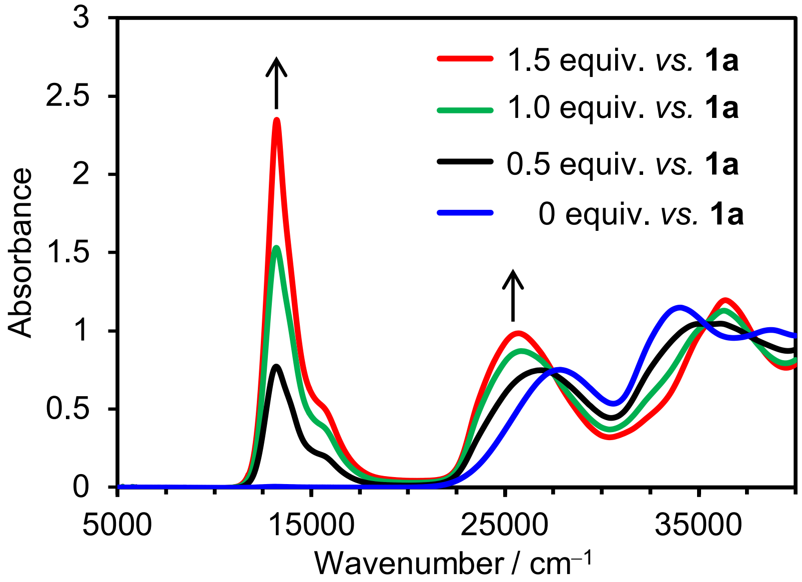


Fig. S20 UV-vis-NIR spectra of **1a** (5.0×10^{-4} M) in the absence and presence of $AgSbF_6$ at 298K in dichloroetahne.

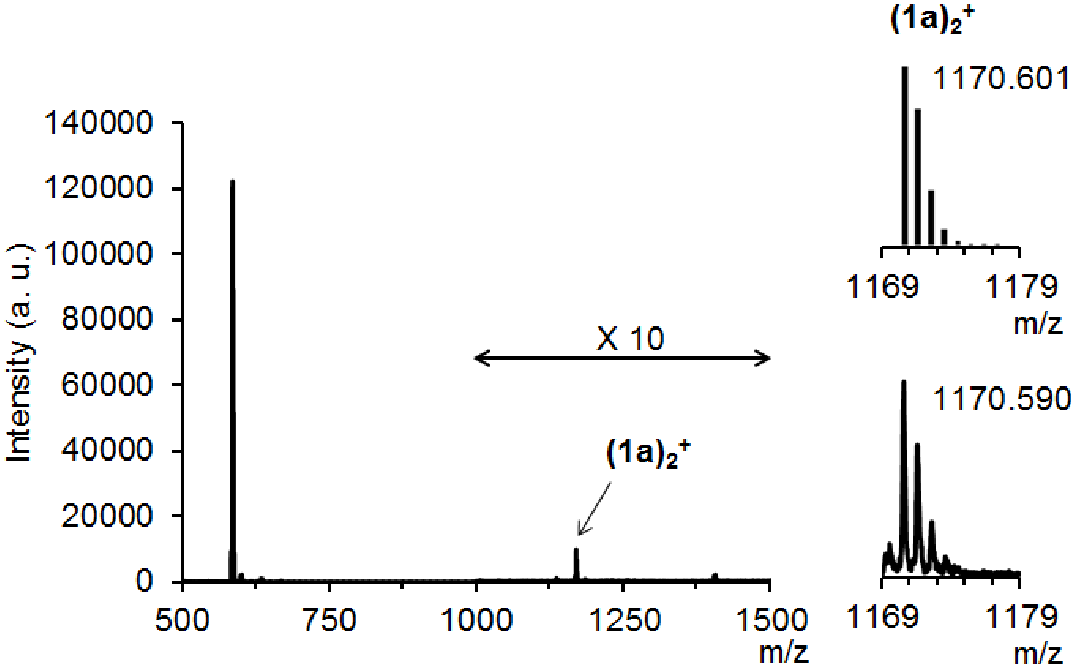
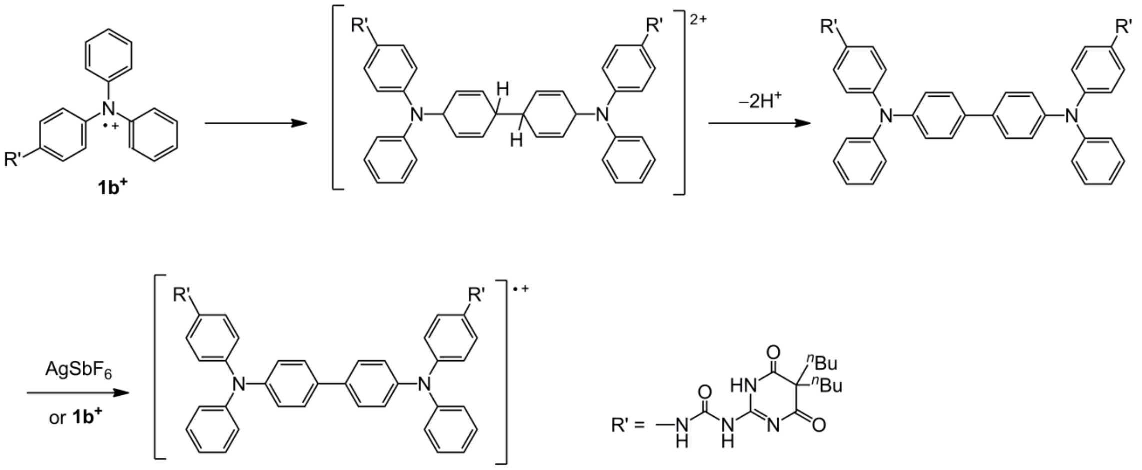


Fig. S21 ESI-TOF-mass spectrum of $(\mathbf{1a})_2^+$ obtained from the reaction of **1a** with 0.5 equiv. of $AgSbF_6$ respect to **1a** in CH_2Cl_2. The intensities in the 1000-1500 m/z were multiplied by a factor of 10. Inset: experimental (bottom) and theoretical (top) isotopic distributions for $(\mathbf{1a})_2^+$.

Scheme S1. Possible mechanism for the formation of the **TPB**$^{\bullet+}$ derivatives from **1b**$^{+}$.



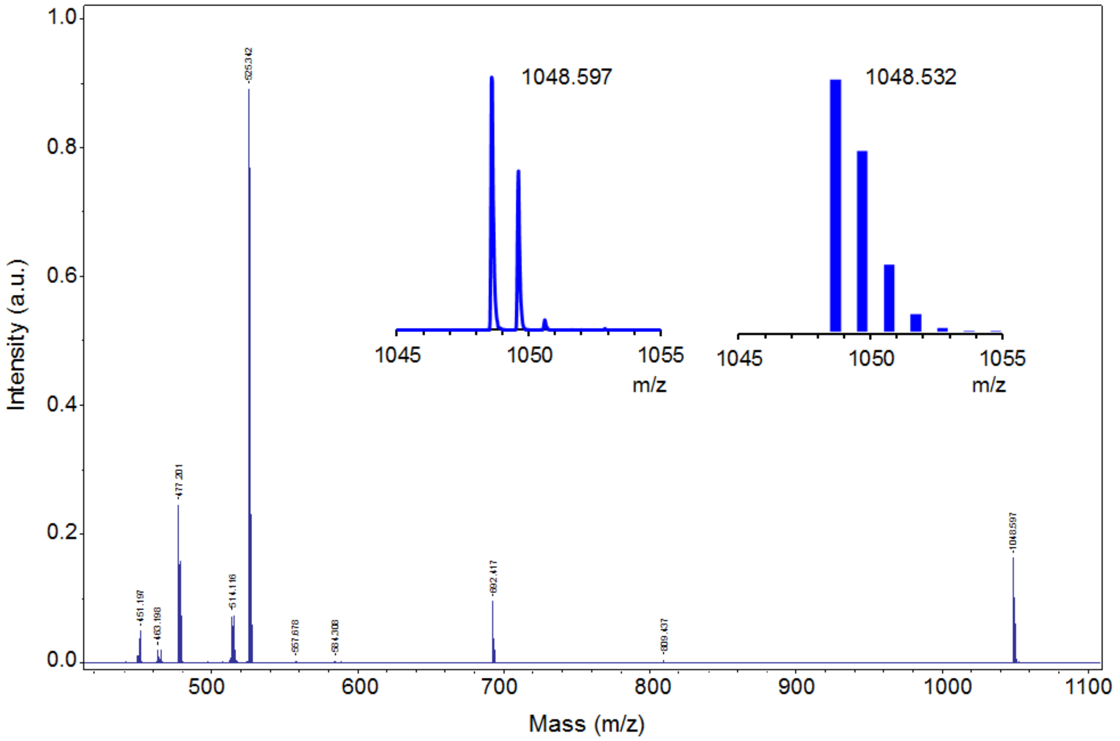


Fig. S22 MALDI-TOF-mass spectrum of the **TPB**$^{\bullet+}$ derivative obtained from the reaction of **1b** with $Cu(ClO_4)_2$ (positive mode, dithranol matrix). Inset: experimental (left) and theoretical (right) isotopic distributions.

References

S1. Baruah, P. K.; Gonnade, R.; Phalgune, U. D.; Sanjayan, G. J. *J. Org. Chem.* **2005**, *70*, 6461-6467.

S2. Lee, W.-Y.; Kurosawa, T.; Lin, S.-T.; Higashihara, T.; Ueda, M.; Chen, W.-C. *Chem. Mater.* **2011**, *23*, 4487-4497.

S3. Gorvin, J. H. *J. Chem. Soc. Perkin Trans. 1* **1988**, 1331-1335.

S4. Kelkar, A. A.; Patil, N. M.; Chaudhari, R. V. *Tetrahedron Lett.* **2002**, *43*, 7143-7146.

S5. Lai, G.; Bhamare, N. K.; Anderson, W. K. *Synlett* **2001**, *2*, 230-231.

S6. Moulin, E.; Niess, F.; Maaloum, M.; Buhler, E.; Nyrkova, I.; Giuseppone, N. *Angew. Chem. Int. Ed.* **2010**, *49*, 6974-6978.

S7. Liou, G.-S.; Lin, H. Y.; Yen, H.-J. *J. Mater. Chem.*, **2009**, 19, 7666-7673.

S8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R. L.Martin, K.Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Gaussian, Inc., Wallingford, CT, 2009.

S9. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.

S10. P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213−222.

S11. (a) Conners, K. A. *Binding Constants: The Measurement of Molecular Complex Stability*; Wiley-Interscience: New York, **1987**. (b) Bisson, A. P.; Carver, F. J.; Eggleston, D. S.; Haltiwanger, R. C.; Hunter, C. A.; Livingstone, D. L.; McCabe, J. F.; Rotger, C.; Rowan, A. E. *J. Am. Chem. Soc.* **2000**, *122*, 8856-8868. (c) Li, X.; Fang, Y.; Deng, P.; Hu, J.; Li, T.; Feng, W. Yuan, Li. *Org. Lett.* **2011**, *13*, 4628-4631.

S12. (a) Song, L.; Trogler, W. C. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 770-772. (b) Connelly, N. G.; Geiger, W. E. *Chem. Rev.*, **1996**, *86*, 877-910.