Supplementary Material (ESI) for Chemical Communications

Amino-substituted rylene dicarboximides and their quinoidal charge delocalization after deprotonation

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Supporting information

General: The solvents and chemicals used were of commercial grade. *N*-(2, 6-diisopropylphenyl)-4-bromo-naphthalene 1,8-dicarboximide (**6**), *N*-(2, 6-diisopropylphenyl)-9-bromo-perylene 3, 4-dicarboximide (**7**), *N*-(2, 6-diisopropylphenyl)-1,6,9,14-tetrakis(4-(1,1,3,3-tetramethylbutyl) phenoxy)-11-bromo-terrylene 3,4-dicarboximide (**8**) and ***N***-(2, 6-diisopropylphenyl)-1,6-bis(4-(1,1,3,3-tetramethylbutyl)phenoxy)-13-bromo-quarterrylene 3, 4-dicarboximide (**9**) were synthesized as previously described [1-3]. Column chromatography was performed on silica gel (Geduran Si_{60}, Merck). ^{1}H, ^{13}C, H, H COSY and NOE NMR were recorded on Bruker DPX 250, DRX 500 and Avance 700 NMR spectrometers. Infrared spectra were obtained on a Nicolet FT IR320. FD mass spectra were recorded with a VG-instruments ZAB 2-SE-FPD instrument. MALDI-TOF mass spectra were recorded on a Bruker MALDI-TOF spectrometer. UV/Vis/NIR spectra were recorded in 1-cm quartz cuvette on a Perkin-Elmer Lambda 900 spectrophotometer. Elemental analyses were performed by the Department of Chemistry and Pharmacy of the University of Mainz.

General procedure for Buchwald condition.

The bromo-RI (0.18 mmol), 4-aminobenzonitrile (0.36 mmol), tris-(dibenzylideneacetone)-dipalladium(0) (17 mg, 0.018 mmol), tris-*tert*-butylphosphine (18 mg, 0.09mmol), sodium-*tert*-butoxide (67 mg, 0.69 mmol) and dry toluene (10 mL) were stirred at 80°C under argon overnight. After cooling, the mixture was evaporated in vacuo and purified by a column chromatography on silica gel using dichloromethane as an eluent.

***N*-(2,6-diisopropylphenyl)-4-((*p*-cyanophenyl)amino)naphthalene 1,8-dicarboximide (2)**

Using **6**, the general procedure afforded the title compound (81 mg, 95%). ^{1}H NMR (700MHz, acetone-d_6, 50°C): δ =8.90(s, N-H, 1H), 8.76 (d, *J*=8.4 Hz, 1H), 8.63(d, *J*=7.2 Hz, 1H), 8.53(d, *J*=8.1 Hz, 1H), 7.87(t, J_1=7.6 Hz, J_2=8.1 Hz, 1H), 7.80(d, *J*=8.1 Hz, 1H), 7.74(d, *J*=8.3 Hz, 2H), 7.54 (d, *J*=8.2 Hz, 2H), 7.42(t, *J*=7.8 Hz, 1H), 7.33(d, *J*=7.8 Hz, 2H), 2.64 (sep, *J*=6.8 Hz, 2H), 1.13(d, *J*=6.8 Hz, 12H); H,H COSY NMR (700MHz, acetone-d_6, 50°C): coupling of δ=(8.76, 8.61, 7.87), (8.53, 7.80), (7.74, 7.54), (7.42, 7.33); ^{13}C-NMR (62.5 MHz, acetone-d_6, 25°C): δ =165.0, 164.3, 147.4, 146.8, 145.8, 134.6, 133.7, 132.7, 132.5, 131.3, 129.8, 129.7, 127.1, 125.4, 124.5, 124.0, 120.0, 119.7, 116.6, 114.4, 105.4, 30.6, 24.2 ppm. IR: ν =3315, 3068, 2962, 2929, 2869, 2219, 1700, 1648, 1575, 1508, 1463, 1357, 1309, 1236, 1164, 1056, 1010, 917, 831, 777 cm^{-1}; UV-Vis (acetone) λ_{max}, nm (ε): 431 (21300); MS (FD): m/z, 473.4 (100%), M+; Found: C, 78.81; H, 5.87; N, 8.47 %. Calc. for $C_{31}H_{27}N_3O_2$: C, 78.62; H, 5.75; N, 8.87 %.

The NMR data of **2'** (deprotonation by NaOH). ^{1}H NMR (500MHz, acetone-d_6, 25°C): δ = 8.83(d, *J*=7.9 Hz, 1H), 8.27(d, *J*=7.4 Hz, 1H), 7.82(d, *J*=9.1 Hz, 1H), 7.47(d, *J*=8.5 Hz, 2H), 7.29(t, *J*=7.7 Hz, 1H), 7.24(t, J_1=7.7 Hz, J_2=7.6 Hz, 1H), 7.21(d, *J*=7.7 Hz, 2H), 7.08(d, *J*=8.5 Hz, 2H), 6.52 (d, *J*=9.1 Hz, 1H), 2.64 (sep, *J*=6.8 Hz, 2H), 1.13(d, *J*=6.8 Hz, 12H).

***N*-(2, 6-diisopropylphenyl)-9-((*p*-cyanophenyl)amino)perylene 3,4-dicarboximide (3a)**

Using **7**, the general procedure afforded the title compound (90 mg, 84%). ^{1}H NMR (700MHz, acetone-d_6, 50°C): δ =8.78(d, *J*=7.5 Hz, 1H), 8.72(d, *J*=8.0 Hz, 1H), 8.70(d, *J*=8.3 Hz, 1H), 8.63(d, *J*=8.0 Hz, 1H), 8.60(d, *J*=8.0 Hz, 1H), 8.58(d, *J*=8.0 Hz, 1H), 8.49(s, 1N-H), 8.35(d, *J*=8.4 Hz, 1H), 7.76-7.74(m, 2H), 7.66(d, *J*=8.5 Hz, 2H), 7.44(t, *J*=7.9 Hz, 1H), 7.36-7.33(m, 4H), 2.83 (sep, *J*=6.8 Hz, 2H), 1.16(d, *J*=6.9 Hz, 12H); H,H COSY NMR (700MHz, acetone-d_6, 50°C): coupling of δ=(8.78, 8.35, 7.76), (8.70, 7.76), (8.72, 8.60), (8.63, 8.58), (7.66, 7.36), (7.44,7.36), (2.83, 1.16); NOE NMR (700MHz, acetone-d_6, 50°C): coupling of δ=(8.78, 8.72), (8.70, 8.63), (8.49, 7.36), (8.49, 8.35), (7.76, 7.36); ^{13}C-NMR (62.5 MHz, CD_2Cl_2 25°C): δ = 164.6, 164.4, 148.0, 146.5, 139.8, 137.8, 134.3, 132.3, 132.12, 132.0, 130.2, 129.7, 128.6, 127.4, 125.7, 125.2, 125.0, 124.7, 124.4, 121.5, 120.8, 120.5, 120.0, 119.7, 118.7, 117.2, 103.6, 29.5, 24.1 ppm. IR: ν =3328, 3064, 2962, 2929, 2867, 2217, 1689, 1644, 1563, 1504, 1351, 1288,

1172, 1058, 971, 910, 804, 750 cm^{-1}; UV-Vis (acetone) λ_{max}, nm (ε): 550(34800); MS (FD): m/z, 598.0 (100%), M^+; Found: C, 81.75; H, 5.42; N, 6.98 %. Calc. for $C_{41}H_{31}N_3O_2$: C, 82.39; H, 5.23; N, 7.03 %.

The NMR data of **3a'** (deprotonation by NaOH). ^{1}H NMR (700MHz, acetone-d_6, 25°C): δ=8.81 (d, *J*=7.7 Hz, 1H), 8.65(d, *J*=7.5 Hz, 1H), 8.29(d, *J*=8.3 Hz, 1H), 8.18(d, *J*=8.4 Hz, 1H), 8.09(d, *J*=8.8 Hz, 1H), 8.06(d, *J*=9.7 Hz, 1H), 7.63(d, *J*=8.6 Hz, 1H), 7.57(d, *J*=8.4 Hz, 2H), 7.45(t, *J*=7.7 Hz, 1H), 7.32(t, *J*=7.6 Hz, 1H), 7.25(d, *J*=7.8 Hz, 2H), 7.10(d, *J*=8.4 Hz, 2H), 6.60(d, *J*=9.4 Hz, 1H), 2.83 (sep, *J*=6.8 Hz, 2H), 1.16(d, *J*=6.9Hz, 12H); H,H COSY NMR (700MHz, acetone-d_6, 25°C): coupling of δ=(8.81, 8.65, 7.45), (8.29, 8.18), (8.09, 7.63), (8.06, 6.60), (7.57, 7.10), (7.32, 7.25), (2.83, 1.16); NOE NMR (700MHz, acetone-d_6, 25°C): coupling of δ=(8.65, 8.18), (8.06, 7.63), (7.10, 6.60).

***N*-(2, 6-diisopropylphenyl)-9-((*p*-octylphenyl)amino)perylene 3,4-dicarboximide (3b)**

Using **7** and *p*-octylaniline instead of 4-aminobenzonitrile, the general procedure afforded the title compound (95 mg, 77%). ^{1}H NMR (700MHz, acetone-d_6, 50°C): δ = 8.75 (d, *J*=7.3 Hz, 1H), 8.63 (d, *J*=8.1 Hz, 1H), 8.55 (d, *J*=7.9 Hz, 1H), 8.54 (d, *J*=8.6 Hz, 1H), 8.50 (d, *J*=8.1 Hz, 1H), 8.48 (d, *J*=8.5 Hz, 1H), 8.42 (d, *J*=8.2 Hz, 1H), 8.12 (s, 1N-H), 7.73 (t, *J*=8.2 Hz, 1H), 7.45 (t, *J*=7.9 Hz, 1H), 7.38 (d, *J*=8.5 Hz, 1H), 7.34 (d, *J*=7.9 Hz, 2H), 7.34 (d, *J*=8.4 Hz, 2H), 7.29 (d, *J*=8.4 Hz, 2H), 2.87-2.70 (sep, *J*=6.8 Hz, 2H), 2.67-2.61 (t, *J*=7.7 Hz, 2H), 1.68-1.62 (t, *J*=7.4 Hz, 2H), 1.34-1.30 (m, 10H), 1.18 (d, *J*=6.9 Hz, 12H), 0.92-0.87ppm (t, *J*=7.1Hz, 3H); H,H COSY NMR (700MHz, acetone-d_6, 50°C): coupling of δ=(7.73, 8.75, 8.48), (7.38, 8.54), (7.29, 7.34), (7.45, 7.34), (8.50, 8.42), (8.55, 8.63), (2.87, 1.18), (2.67, 1.68), (1.62, 1.34), (1.30, 0.92); ^{13}C-NMR (62.5 MHz, CD_2Cl_2 25°C): δ =164.71, 164.55, 146.52, 144.34, 139.16, 138.96, 138.71, 138.17, 132.27, 131.88, 131.07, 129.97, 129.76, 129.16, 129.56, 129.16, 126.68, 126.47, 126.47, 125.11, 125.02, 124.35, 123.61, 121.84, 120.92, 120.83, 119.88, 118.69, 118.48, 111.08, 35.74, 32.30, 32.06, 29.89, 29.73, 29.69, 29.45, 24.14, 24.10, 23.08, 14.27 ppm. IR: ν = 3372, 2964, 2924, 2854, 1690, 1650, 1566, 1514, 1354, 1284, 804,750 cm-1; UV-Vis (acetone) λ_{max}, nm (ε):

596 (35233); MS (FD): m/z 683.5 (100%), M^+; Found: C, 83.39; H, 7.06; N, 3.96 %. Calc. for $C_{48}H_{48}N_2O_2$: C, 84.17; H, 7.06; N, 4.09 %.

The NMR data of **3b'** (deprotonation by NaOH): ^{1}H NMR (250MHz, acetone-d_6, 25 °C): δ = 8.83 (d, *J*=7.6 Hz, 1H), 8.67 (d, *J*=8.5 Hz, 1H), 8.25 (d, *J*=8.5 Hz, 1H), 8.11 (d, *J*=8.7 Hz, 1H), 7.99 (d, *J*=9.0 Hz, 1H), 7.94 (d, *J*=10.1 Hz, 1H), 7.48 (d, *J*=9.0 Hz, 1H), 7.46 (t, *J*=7.7 Hz, 1H), 7.32 (t, *J*=7.9 Hz, 1H), 7.25 (d, *J*=7.9 Hz, 2H), 7.16 (d, *J*=8.4 Hz, 2H), 6.89 (d, *J*=8.4 Hz, 2H), 6.52 (d, *J*=10.0 Hz, 1H), 2.77-2.66 (sep, *J*=6.9 Hz, 4H), 2.63-2.56 (t, *J*=7.4 Hz, 2H), 1.64-1.59 (t, *J*=7.4 Hz, 2H), 1.34-1.30 (m, 10H), 1.13-1.10 (d, *J*=6.9 Hz, 12H), 0.92-0.86 ppm (t, *J*=7.0 Hz, 3H); H,H COSY NMR (700MHz, acetone-d_6, 25°C): coupling of δ=(7.50, 8.83, 8.67), (6.87, 7.12), (6.52, 6.48), (7.35, 7.25), (7.99, 7.48), (8.11, 8.25), (2.77, 1.13), (2.63, 1.64), (1.64, 1.34), (1.30, 0.92).

***N*-(2, 6-diisopropylphenyl)-1,6,9,14-tetrakis(4-(1,1,3,3-tetramethylbutyl)phenoxy)-11-((*p*-cyanophenyl)amino)terrylene 3,4-dicarboximide (4)**

Using **8**, the general procedure afforded the title compound (28 mg, 55%). ^{1}H NMR (250MHz, acetone-d_6, 25°C): δ =9.50-9.45 (dd, 2H), 9.22-9.13 (dd, 2H) 8.35(d, *J*=8.9Hz, 1H), 8.17(d, *J*=8.9Hz, 1H), 7.68-7.52(m, 10H), 7.46(d, *J*=7.2Hz, 2H), 7.38-7.28(m, 7H), 7.39-7.11(m, 6H), 2.92(sep, *J*=6.8Hz, 2H), 1.95-1.89 (q, 8H), 1.55-1.49 (q, 24H), 1.23-1.19 (q, 12H), 1.01(d, *J*=6.9Hz, 12H), 0.86-0.83ppm (q, 24H); IR: ν = 3326, 3054, 2952, 2923, 2865, 2221, 1698, 1594, 1502, 1365, 1303, 1211, 1170, 1052, 1014, 958, 829, 727 cm^{-1}; UV-Vis (acetone) λ_{max}, nm (ε): 668(41900); MS (FD): m/z, 1539.3 (100%), M^+.

***N*-(2, 6-diisopropylphenyl)-1,6-bis(4-(1,1,3,3-tetramethylbutyl)phenoxy)-13-((*p*-cyanophenyl) amino)quarterrylene 3,4-dicarboximide (5)**

Using **9**, the general procedure afforded the title compound (25 mg, 53%). IR: ν =3359, 3054, 2954, 2925, 2865, 2211, 1693, 1577, 1500, 1384, 1317, 1265, 1209, 1170, 1064, 1014, 806, 744 cm^{-1}; UV-Vis (acetone) λ_{max}, nm (ε): 751(51200); MS (FD): m/z, 1255.3 (100%), M^+.

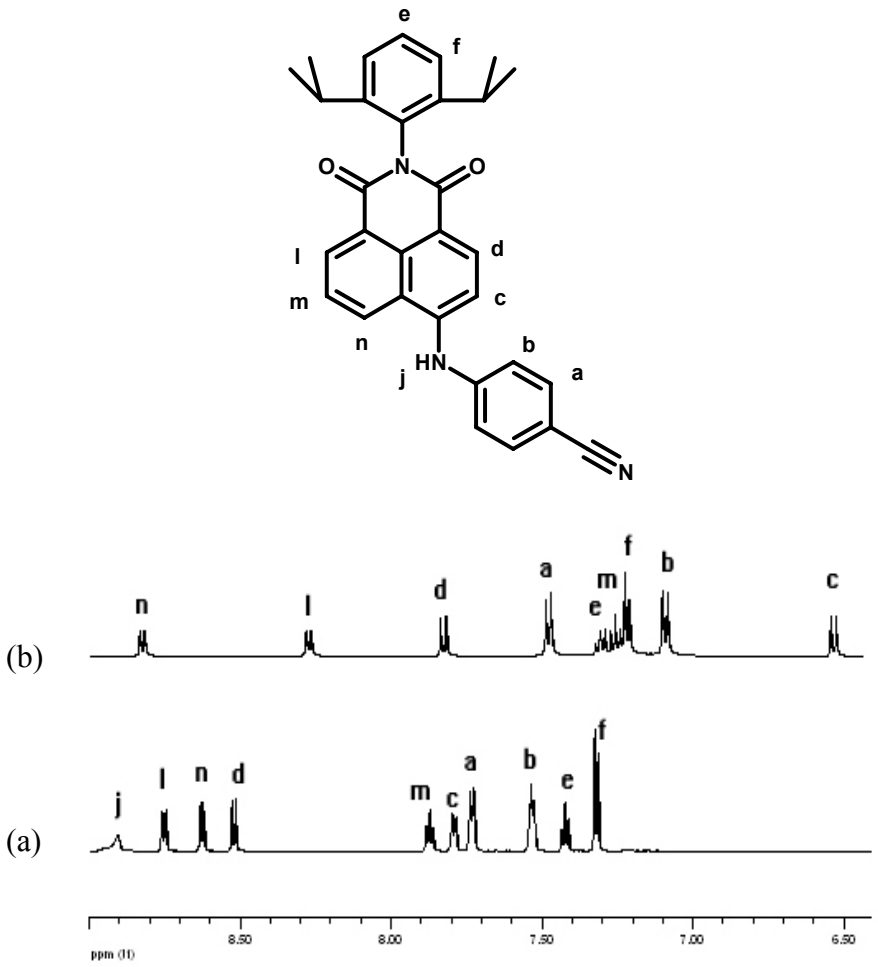

Fig. S1. ^{1}H NMR spectra of **2** and **2'** (after deprotonation by NaOH): in acetone-d_6.

Table S1. Chemical shifts and H,H coupling constants of **2** before or after deprotonation in acetone-d6.

Proton / Items	H_a	H_b	H_c	H_d	H_e	H_f	H_j	H_l	H_m	H_n
δ_1, ppm	7.74	7.54	**7.80**	**8.53**	7.42	7.33	8.91	8.76	7.87	8.63
J_1, Hz	8.3	8.3	**8.1**	**8.1**	7.8	7.8		8.4		7.2
δ_2, ppm	7.47	7.08	**6.52**	**7.82**	7.29	7.21		8.27	7.24	8.83
J_2, Hz	8.5	8.5	**9.1**	**9.1**	7.7	7.7		7.4		7.9
δ_1-δ_2, ppm	0.27	0.44	**1.28**	**0.71**	0.13	0.12		0.49	0.63	-0.20

δ_1, δ_2, J_1 and J_2 denote the chemical shift and H,H coupling constants before and after deprotonation, respectively.

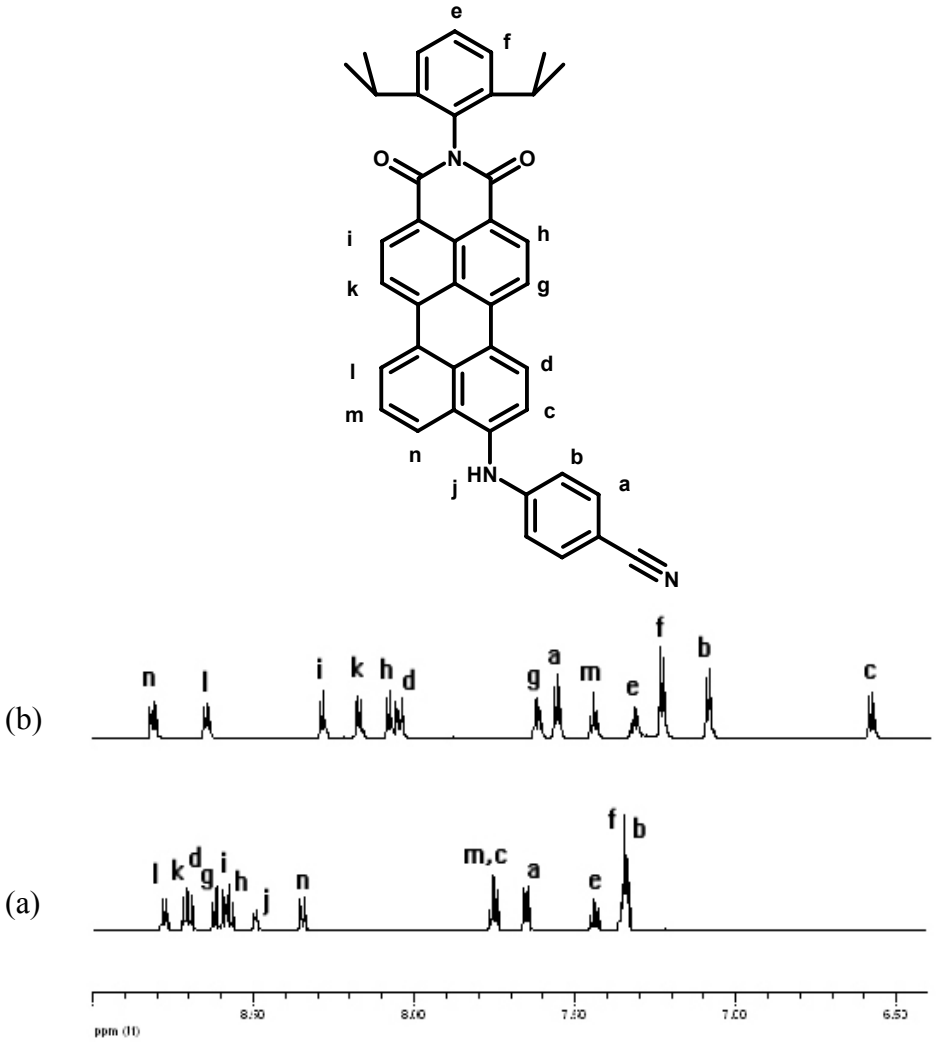

Fig. S2. ^{1}H NMR spectra of **3a** and **3a'** (after deprotonation by NaOH) in acetone-d_6

Table S1. Chemical shifts and H,H coupling constants of **3a** before or after deprotonation in acetone-d6.

Proton / Items	H_a	H_b	H_c	H_d	H_e	H_f	H_g	H_h	H_i	H_j	H_k	H_l	H_m	H_n
δ_1, ppm	7.66	7.35	**7.75**	**8.70**	7.44	7.35	**8.62**	**8.58**	8.60	8.49	8.72	8.78	7.75	8.35
J_1, Hz	8.5	8.5	**8.3**	**8.3**	7.9	7.9	**8.0**	**8.0**	8.0		8.0	7.5		8.4
δ_2, ppm	7.57	7.10	**6.60**	**8.06**	7.32	7.25	**7.63**	**8.09**	8.29		8.18	8.65	7.45	8.81
J_2, Hz	8.4	8.4	**9.4**	**9.7**	7.6	7.8	**8.6**	**8.8**	8.3		8.4	7.5		7.7
δ_1-δ_2, ppm	0.09	0.25	**1.15**	**0.64**	0.12	0.10	**0.99**	**0.49**	0.11		0.54	0.13	0.30	-0.46

δ_1, δ_2, J_1 and J_2 denote the chemical shift and H,H coupling constants before and after deprotonation, respectively.

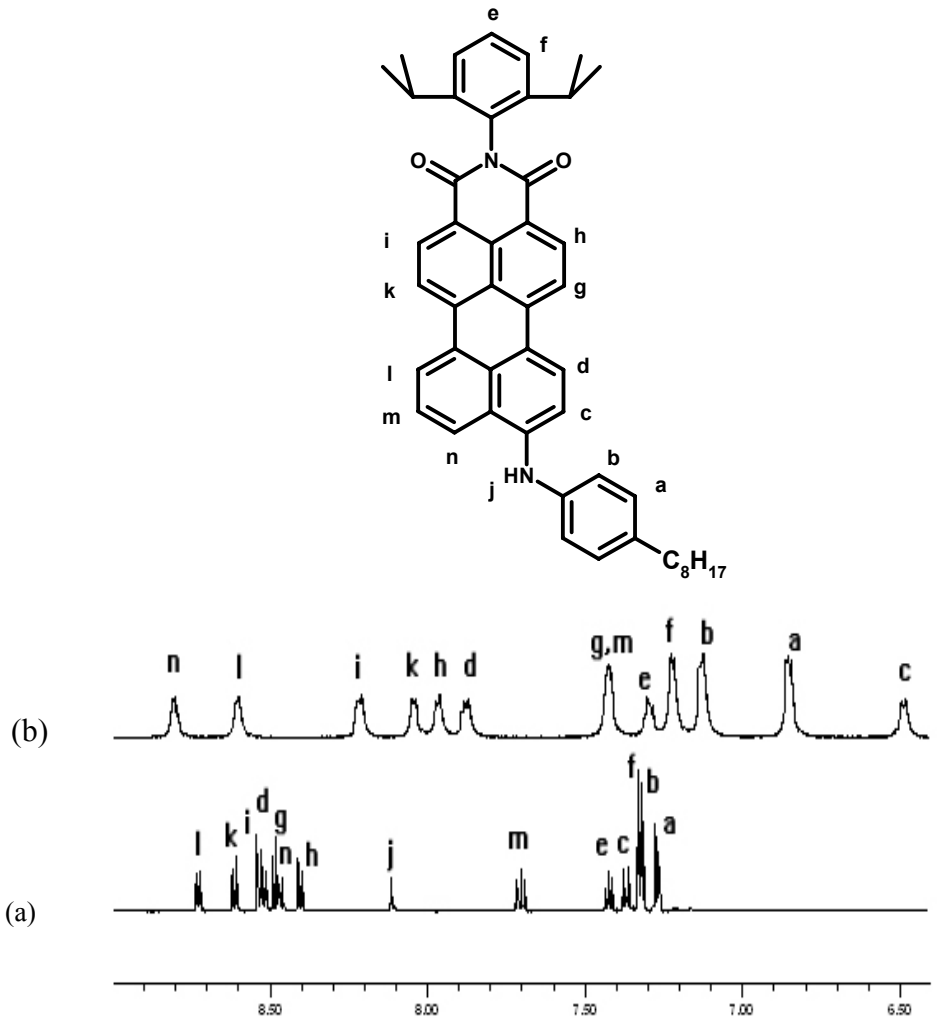

Fig. S3. ^{1}H NMR spectra of **3b** and **3b'** (after deprotonation by NaOH) in acetone-d_6.

Table S1. Chemical shifts and H,H coupling constants of **3b** and **3b'** (after deprotonation by NaOH) in acetone-d_6.

Proton / Items	H_a	H_b	H_c	H_d	H_e	H_f	H_g	H_h	H_i	H_j	H_k	H_l	H_m	H_n
δ_1, ppm	7.29	7.34	**7.38**	**8.54**	7.44	7.34	**8.50**	**8.42**	8.55	8.12	8.63	8.75	7.71	8.48
J_1, Hz	8.4	8.4	**8.5**	**8.5**	7.9	7.9	**8.2**	**8.2**	8.1		8.1	7.3		8.5
δ_2, ppm	6.87	7.16	**6.52**	**7.94**	7.35	7.25	**7.48**	**7.99**	8.25		8.11	8.67	7.46	8.83
J_2, Hz	8.2	8.2	**10.0**	**10.0**	7.5	7.5	**9.0**	**9.0**	8.5		8.5	8.5		7.6
δ_1-δ_2, ppm	0.42	0.18	**0.86**	**0.60**	0.09	0.09	**1.02**	**0.43**	0.30		0.50	0.08	0.25	-0.35

δ_1, δ_2, J_1 and J_2 denote the chemical shifts and H,H coupling constants before and after deprotonation, respectively.

For comparison, the absorption spectrum of the radical cation of **3b**, generated by chemical oxidation with $SbCl_5$ following the previously reported procedure [4], was measured. It shows a sharp absorption peak at 710 nm and a very broad and weak band above 1000 nm in the NIR region.

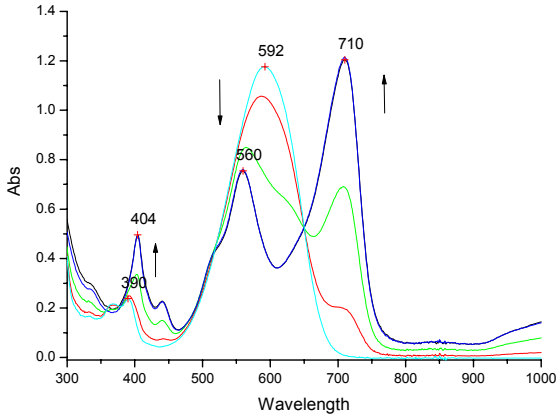

Fig. S4. The absorption spectra of the radical cation of **3b** generated by chemical oxidization upon more and more $SbCl_5$ addition. ($SbCl_5$ stock solution in dichloromethane is 0.001M)

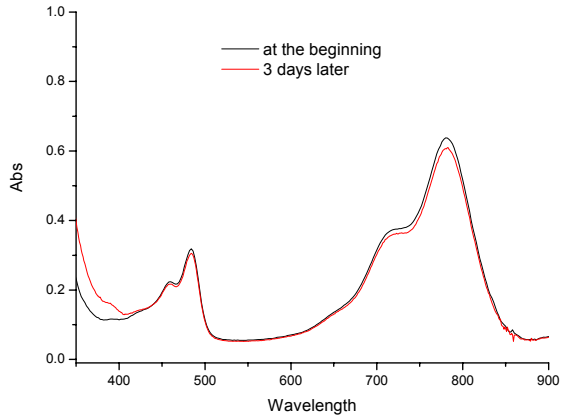

Fig. S5. The absorption change of **3b** deprotonated by BuONa in acetone after 3 days

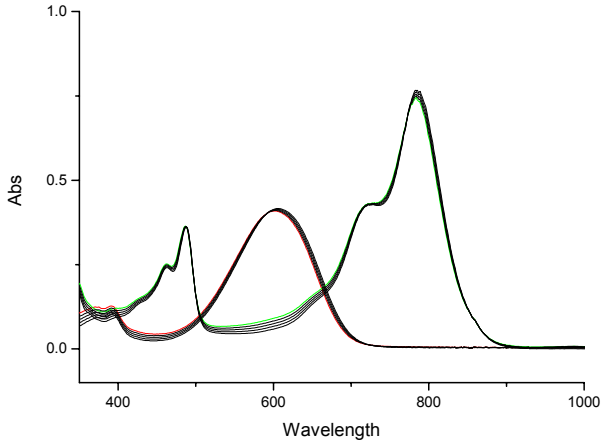

Figure S6. Absorption switches of **3b** in acetone for 5 cycles

Refernces

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3. Y. Avlasevich, K. Müllen, *J. Org. Chem*. 2007, 72, 10243-10246.

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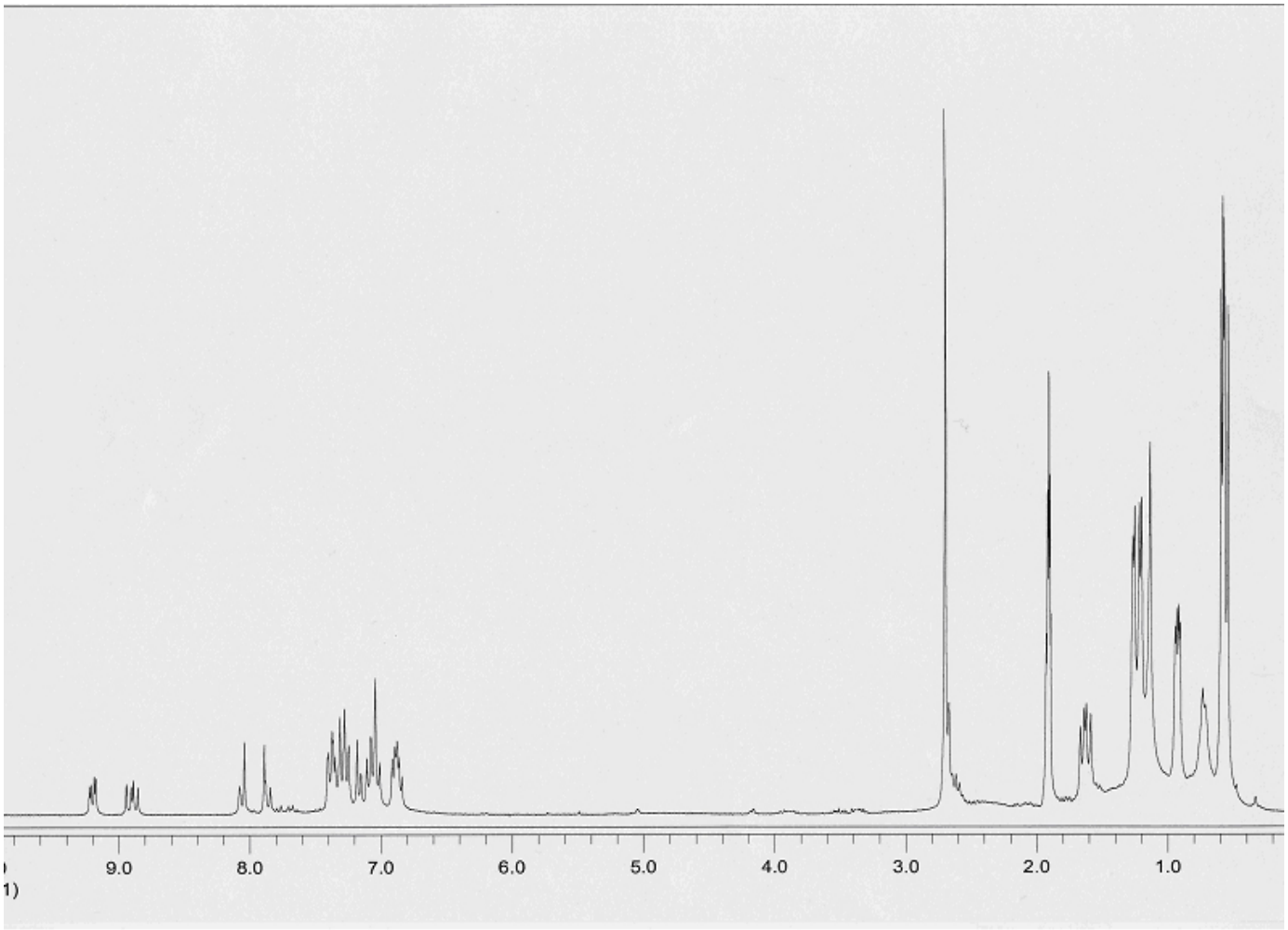
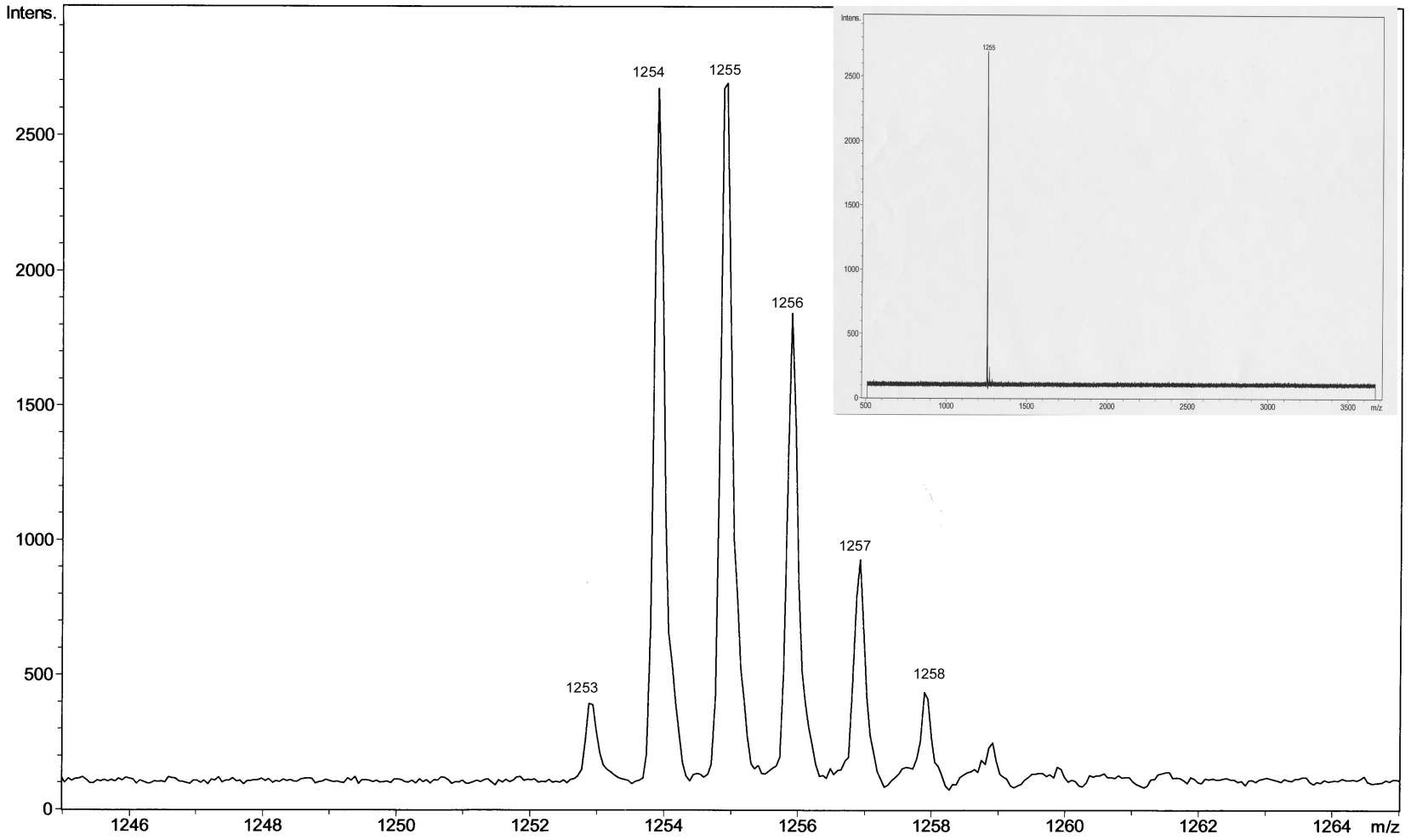
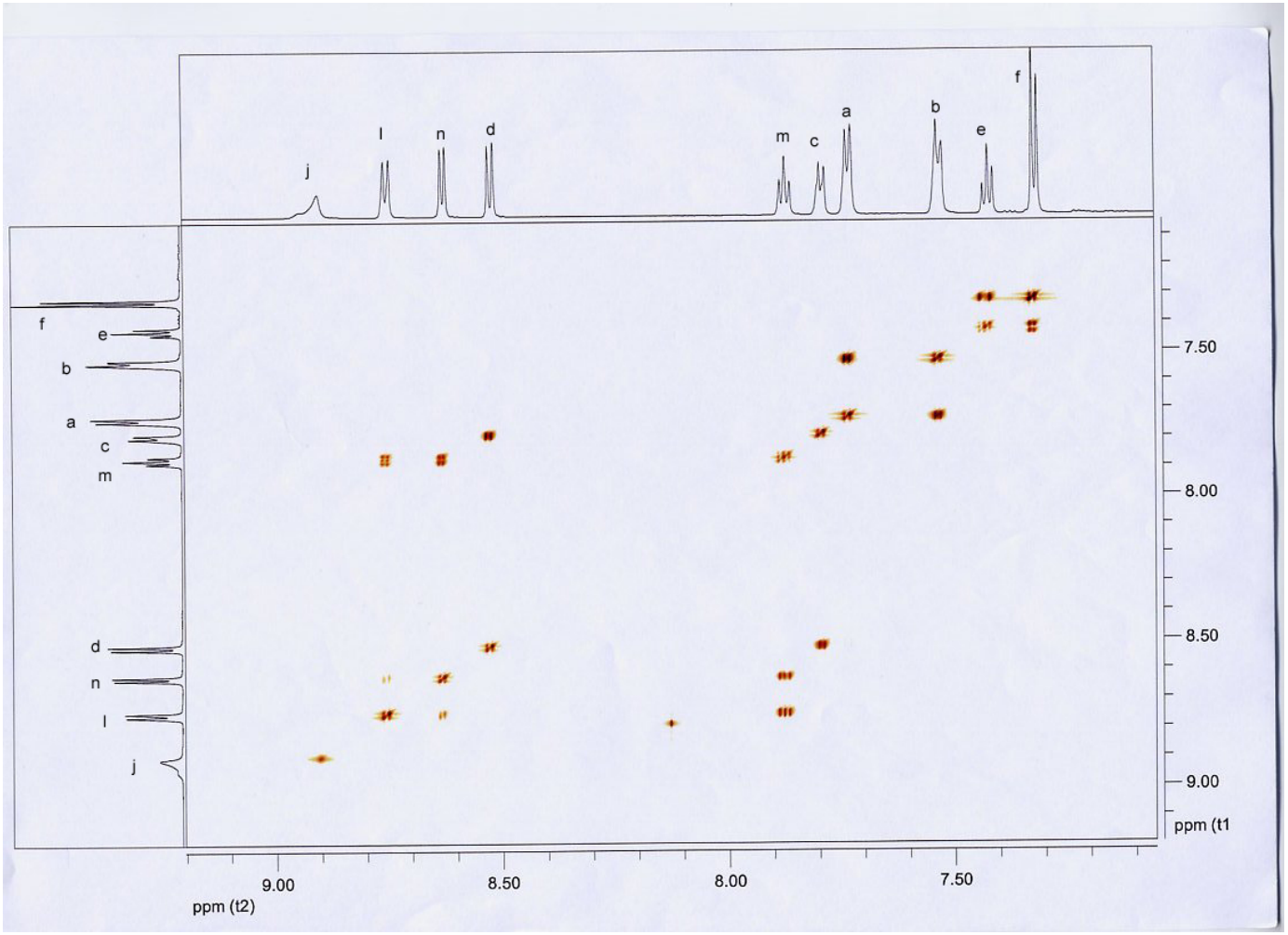


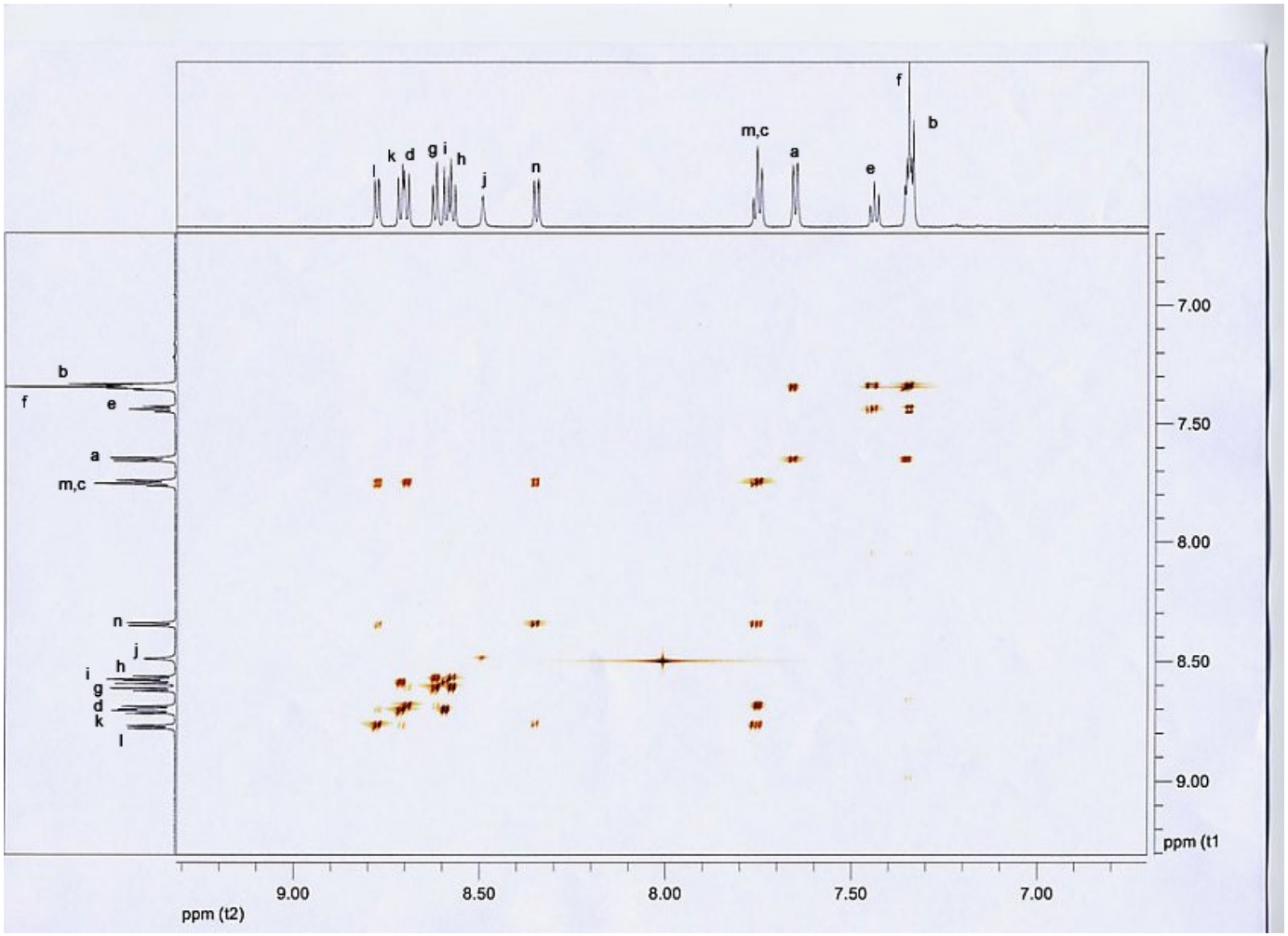
^{1}H NMR (250 MHz, 25 °C) spectrum of **4** in acetone-d_6



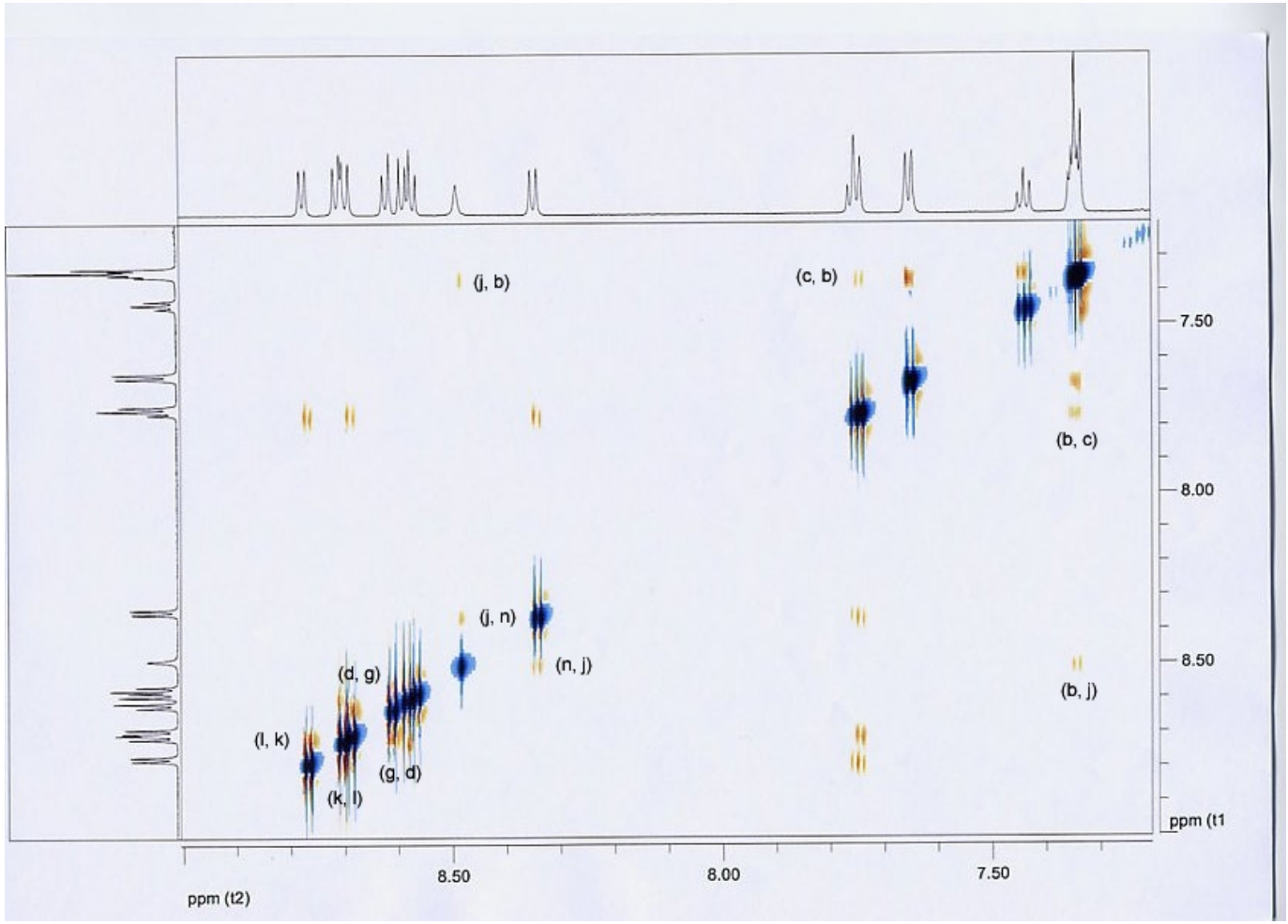
MALDI-TOF-MS spectrum of **5**



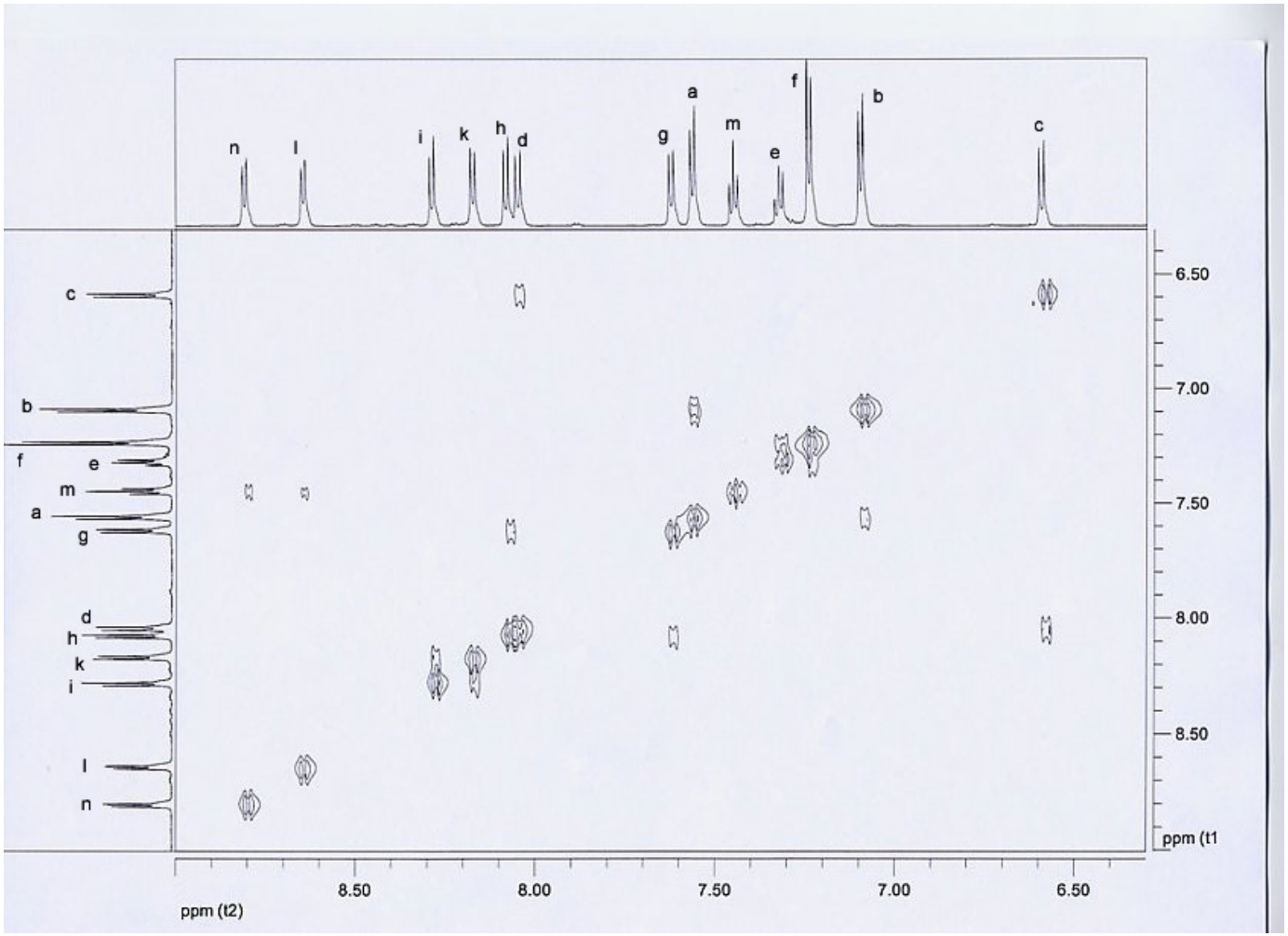
H, H COSY NMR (700MHz, 50°C) spectrum of **2** in acetone-d_6.



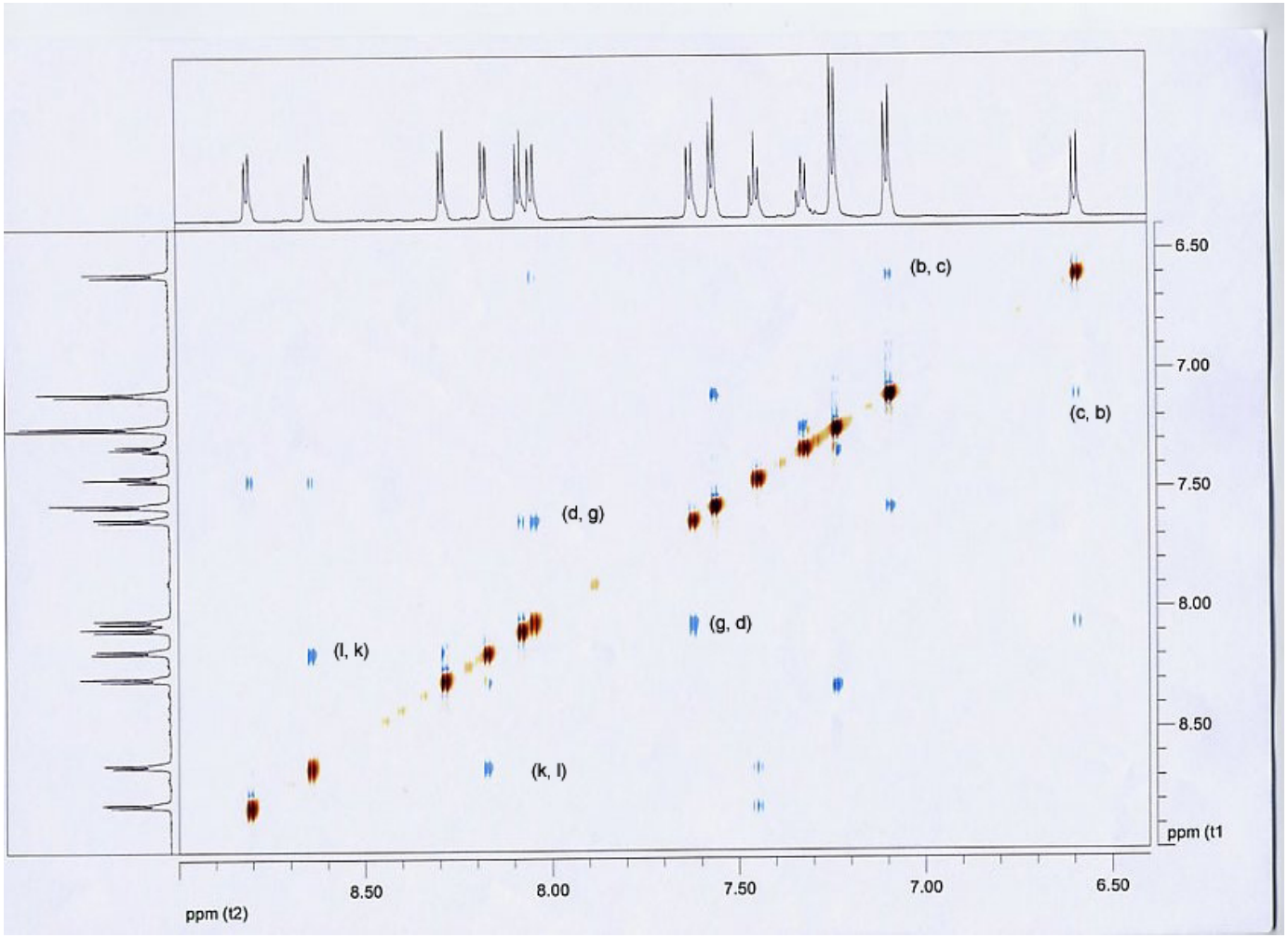
H, H COSY NMR (700MHz, 50°C) spectrum of **3a** in acetone-d_6.



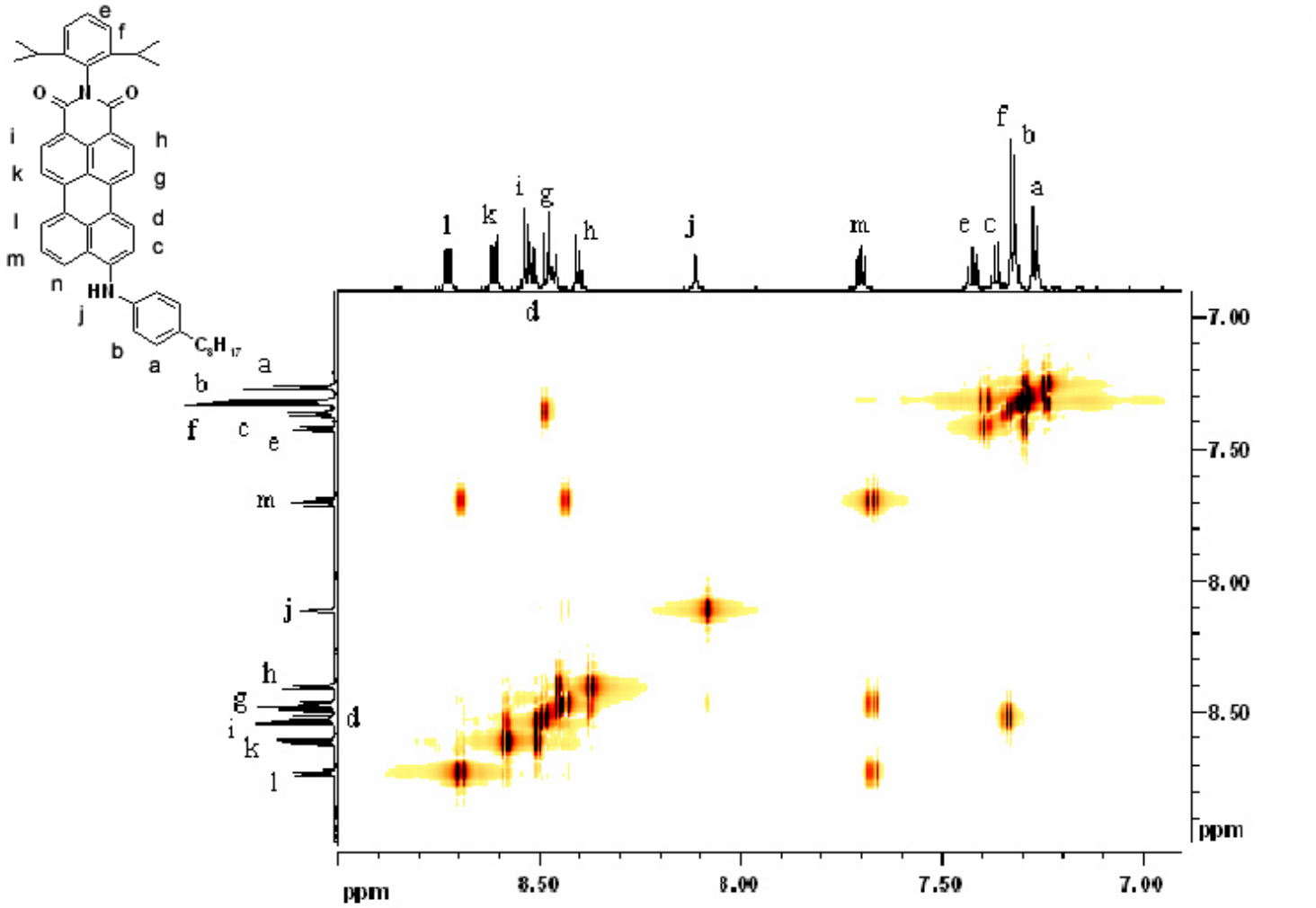
NOE NMR (700MHz, 50°C) spectrum of **3a** in acetone-d_6



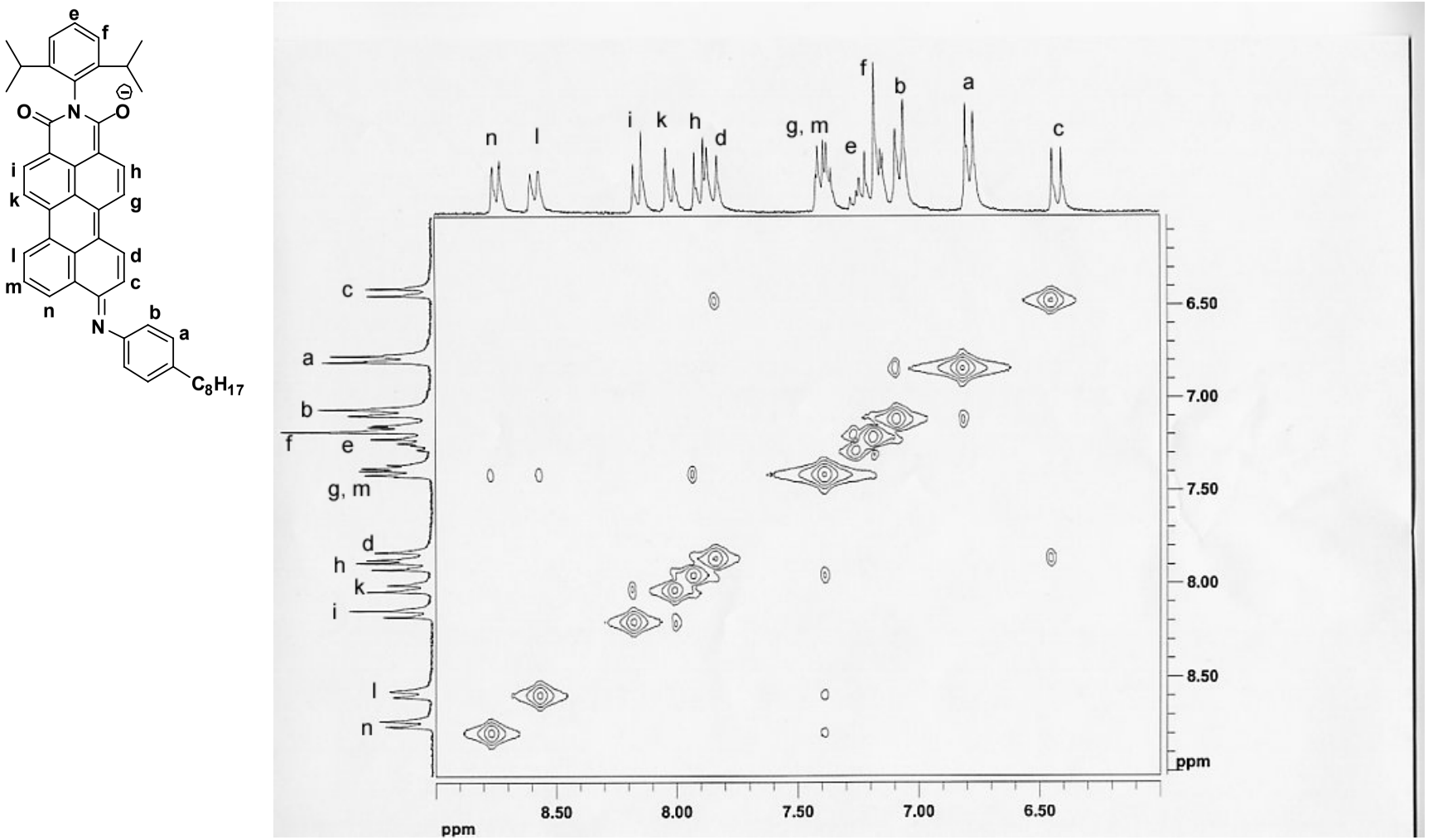
H, H COSY NMR (700MHz, 25°C) spectrum of **3a'** (deprotonated by NaOH) in acetone-d_6



NOE NMR (700MHz, 25°C) spectrum of **3a'** (deprotonated by NaOH) in acetone-d_6



H, H COSY NMR (700MHz, 50°C) spectrum of **3b** in acetone-d_6



H, H COSY NMR (700MHz, 25°C) spectrum of **3b'** (deprotonated by NaOH) in acetone-d_6