Synthesis and Photophysical Characterization of a Subphthalocyanine Fused Dimer – C_{60} Dyad

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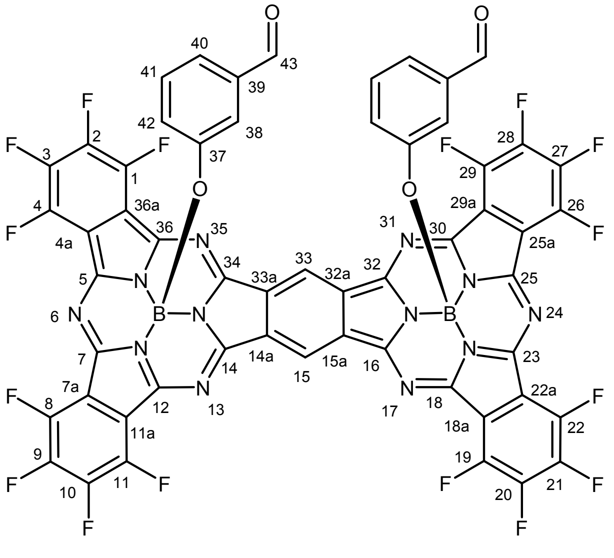
SUPPORTING INFORMATION

General Remarks:

UV/Vis spectra were recorded with a Hewlett-Packard 8453 instrument. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. HRMS spectra were determined on a VG AutoSpec instrument. MALDI-TOF MS were recorded with a Bruker Reflex III spectrometer. NMR spectra were recorded with a BRUKER AC-300 instrument and a BRUKER DRX-500 instrument. Column chromatographies were carried out on silica gel Merck-60 (230-400 mesh, 60 Å), and TLC on aluminum sheets precoated with silica gel 60 F_{254} (E. Merck). Chemicals were purchased from Aldrich Chemical Co. and used as received without further purification.

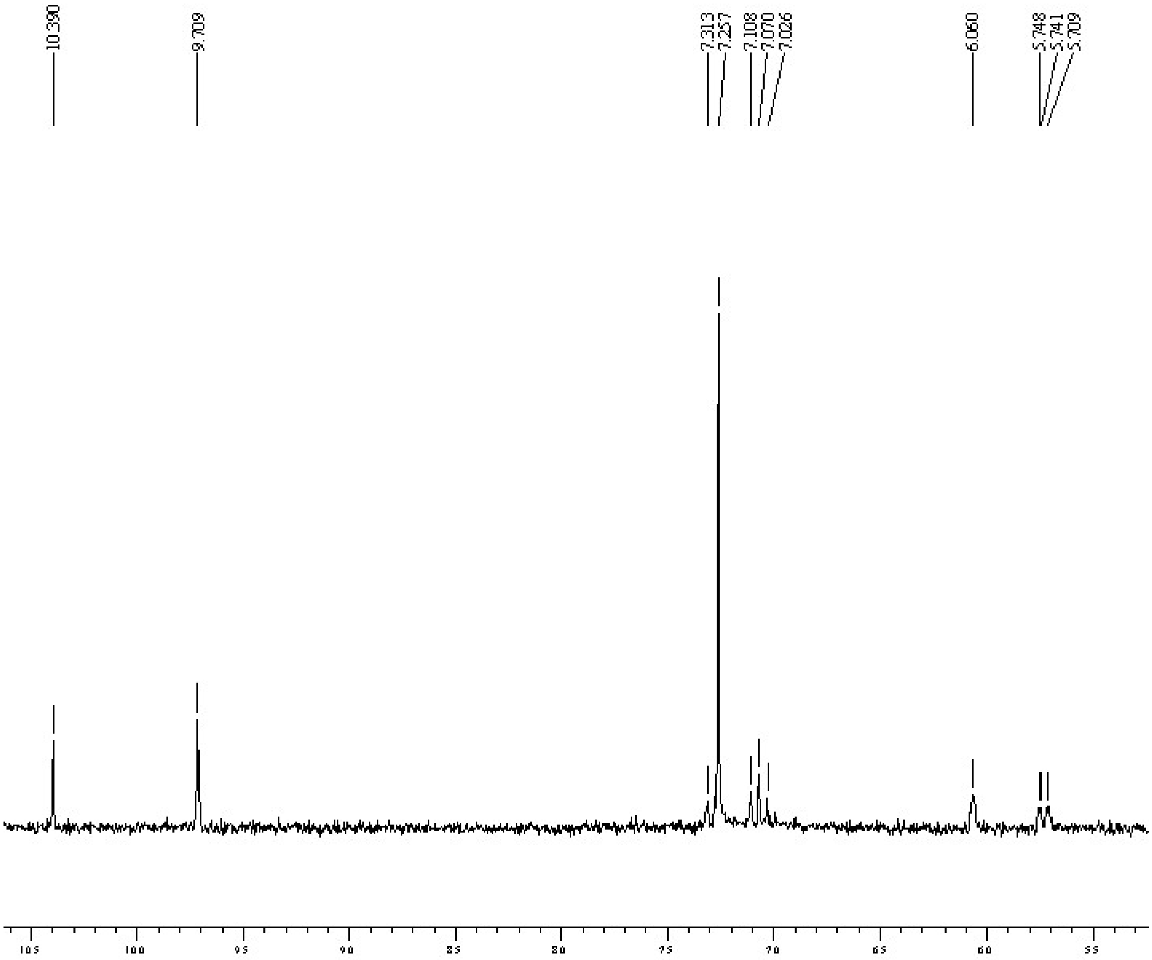
Supplementary data for:

COMPOUND 3a

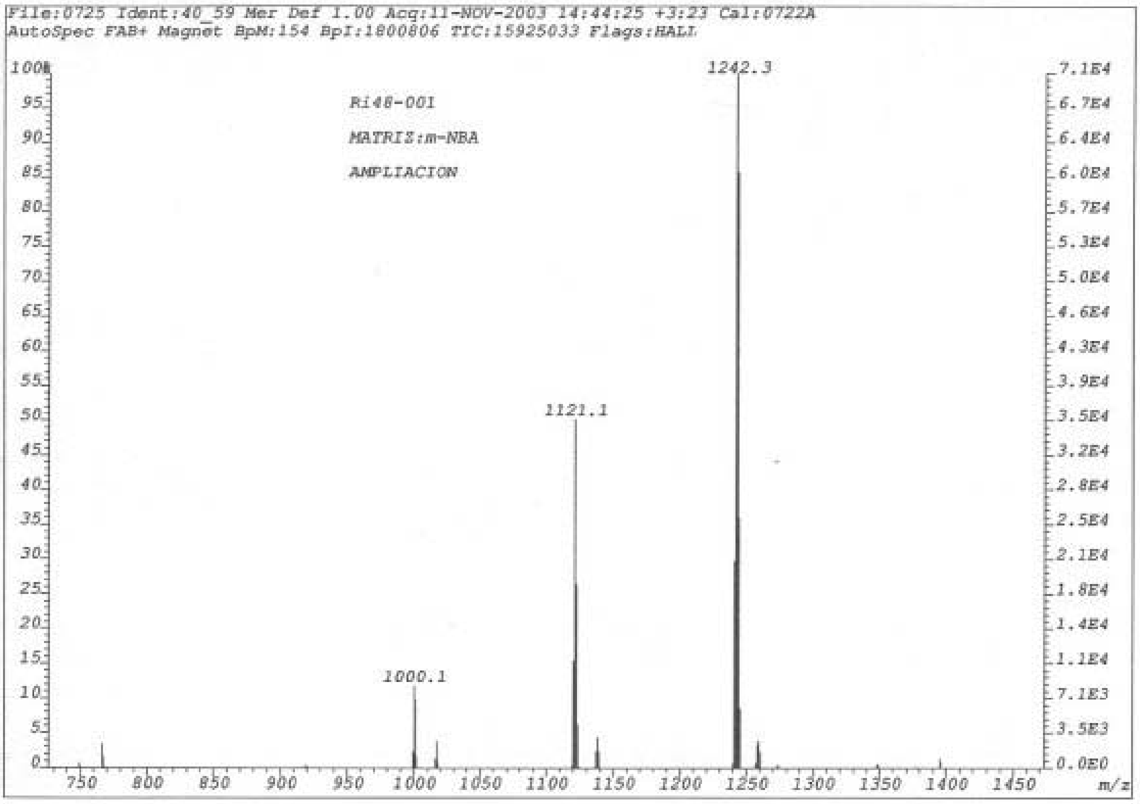


Compound 3a: To a 25 ml round-bottom two-neck flask equipped with a reflux condenser and magnetic stirrer, a 1.0 M solution of BCl_3 (5.5 ml g, 5.5 mmol, 11 eq) in *p*-xylene was added to a mixture of 1,2,4,5-tetracyanobenzene (0.090 g, 0.5 mmol, 1 eq) and tetrafluorophthalonitrile (1g, 5 mmol, 10 eq) under argon atmosphere. The mixture heated at *p*-xylene reflux (136-138°C) for 1-2 hours. The reaction crude was then cooled down to room temperature and flushed with argon. After evaporation of *p*-xylene, 3-hydroxybenzaldehyde was added in excess (1.1 g, 9.1 mmol, 10:1 proportion with respect to a 100% yield). The reaction was carried without solvent in molten 3-hydroxybenzaldehyde, for 1-2 h at 110°C. After cooling down to room temperature, the excess of phenol was removed by washing the crude with a methanol/water 1:1 solution. After purification by column chromatography in silica gel using hexane/dichloromethane/acetone 4:2:1 as eluent, compound **4a** was collected as a dark blue solid, 30 mg (5% with respect to 1,2,4,5-tetracyanobenzene); m.p. > 250ºC; ^{1}H-NMR ($CDCl_3$, 298K, 200 MHz): δ(ppm) = 10.39 (s, 2H, H-15, H-33), 9.71 (s, 2H, H-43), 7.29 (d, J_o = 7.9 Hz, 2H, H-40), 7.07 (t, J_o = 7.8 Hz, 2H, H-41), 6.06 (s, 2H, H-38), 5.72 (dd, J_o = 7.8 Hz, J_m = 1.4 Hz, 2H, H-42); FT-IR (KBr), $\bar{\nu}$ (cm^{-1}): 1636 (C=O), 1534, 1483 (C-N), 1105, 1082; UV-Vis ($CHCl_3$): λ_{max}(nm) (log ε (dm^{3}mol^{-1}cm^{-1})): 691 (5.0), 660 (4.4), 633 (4.5), 603 (4.5), 590 (sh), 490 (3.9), 450 (3.8), 319 (4.6); MALDI-TOF (*m*-NBA): *m/z* = 1242 $[M]^+$, 1121 [M-one axial group]$^+$, 1000 [M-two axial groups]$^+$; HRMALDI calcd for $C_{56}H_{12}B_2N_{12}O_4F_{16}$: $[M^+]$: *m/z*: 1242.103510, found 1242.105010; elemental analysis calcd (%) for $C_{56}H_{12}B_2N_{12}O_4F_{16}$: C 54.14, H 0.97, N 13.53; found C 53.85, H 1.05, N 14.23.

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K)



MALDI-TOF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90
85
80
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70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
7.1E4
6.7E4
6.4E4
6.0E4
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800
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900
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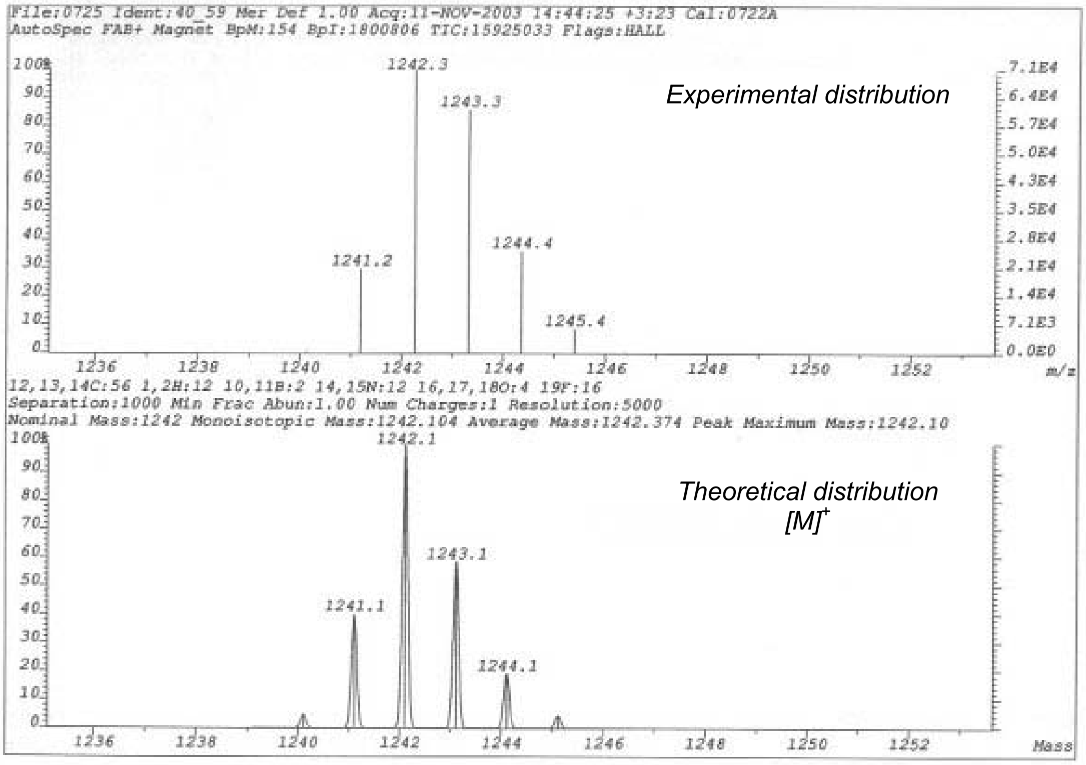
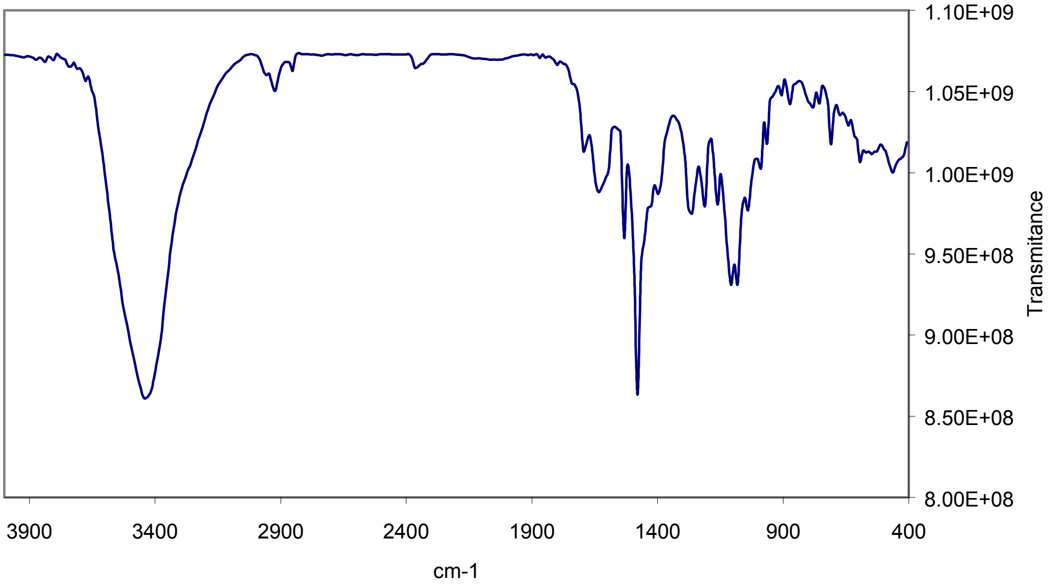
1100
1150
1200
1250
1300
1350
1400
1450
m/z

HRMALDI (Isotopic pattern)



FT-IR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Transmitance
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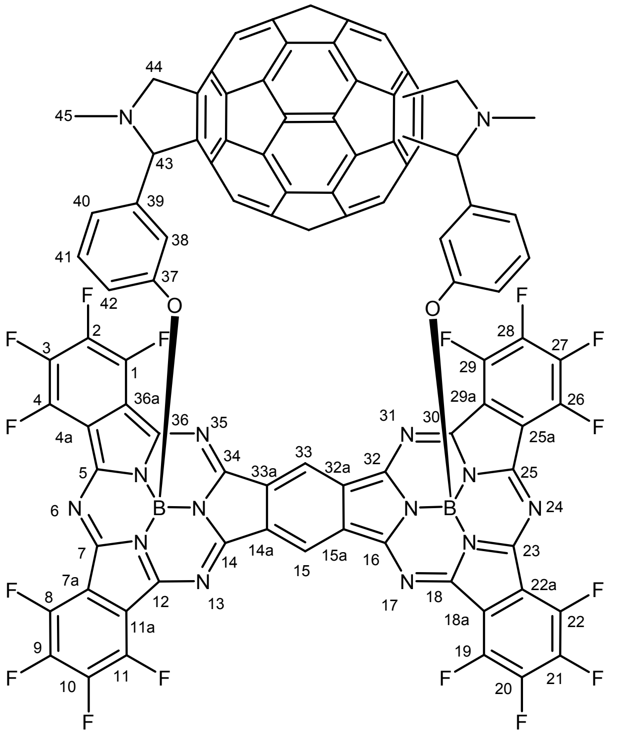
3400
2900
2400
1900
1400
900
400
cm-1

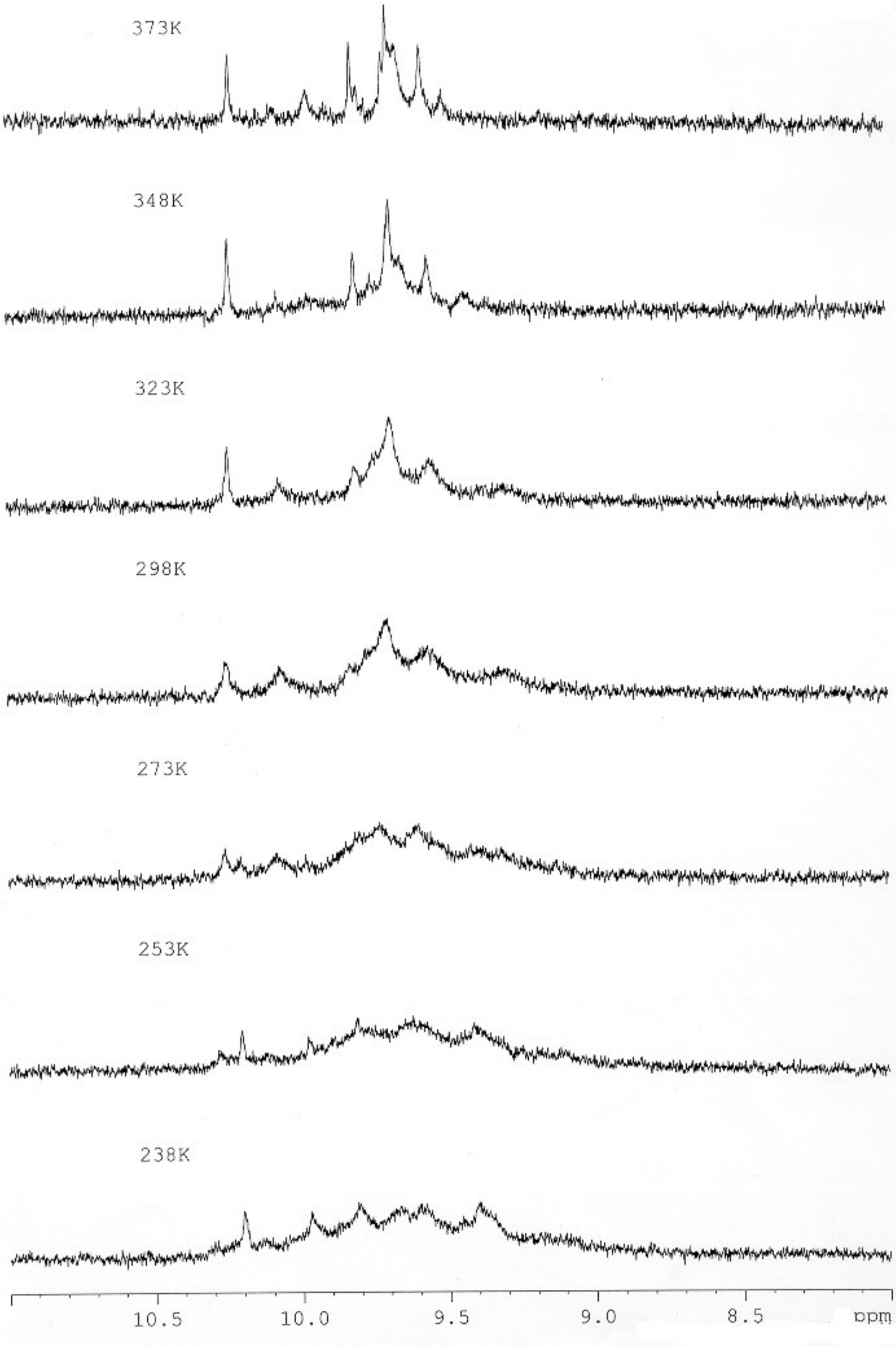
Supplementary data for:

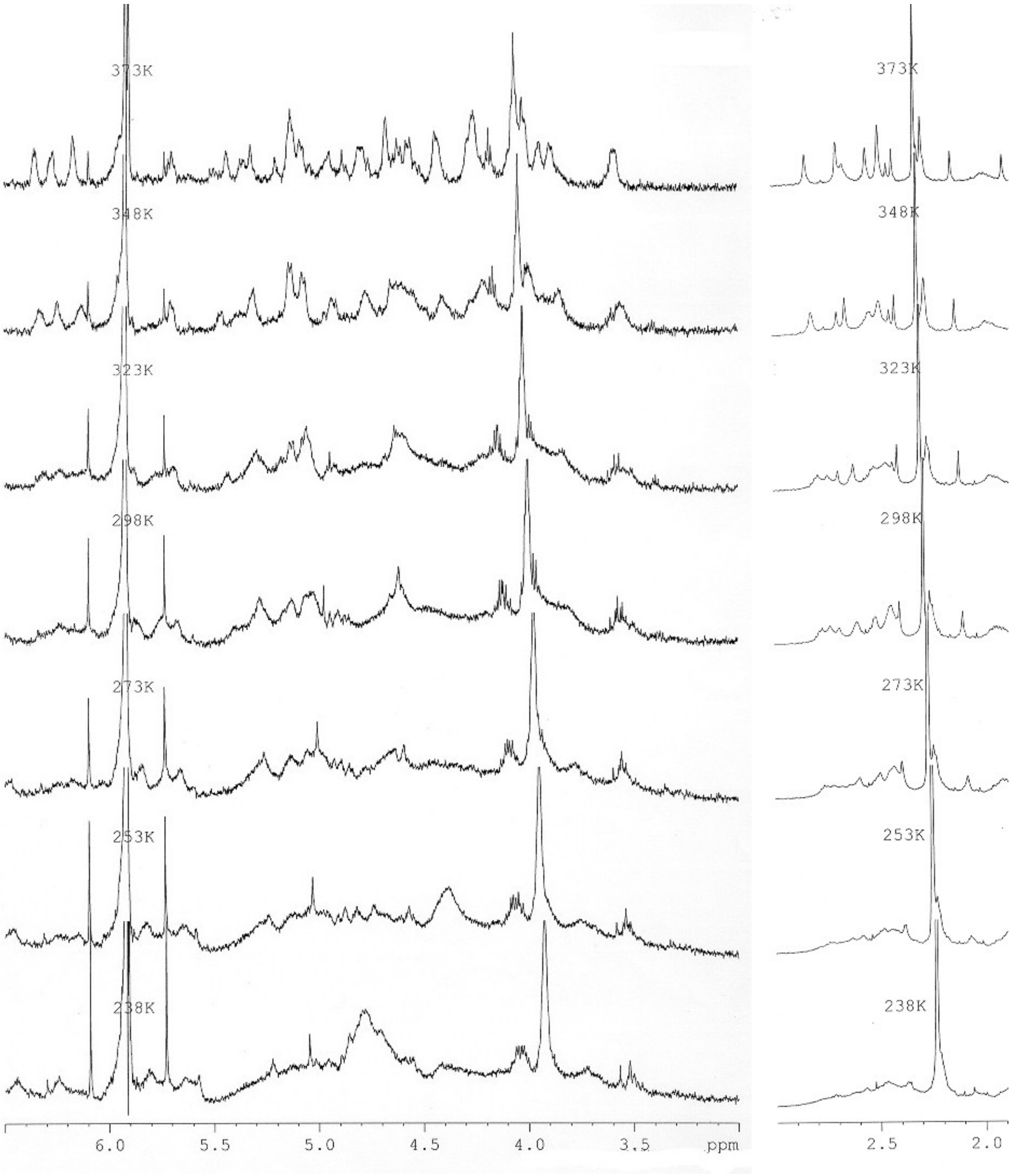
COMPOUND 1



Compound 1: A dry toluene solution (40 mL) of 45 mg (0.04 mmol) of compound **3a**, 52 mg (0.07 mmol) of C_{60}-fullerene, and 20 mg (0.22 mmol) of sarcosine (*N*-methylglycine) was heated to reflux under argon atmosphere for 18 h. The solution was then cooled down to room temperature and the solvent evaporated in *vacuo*. The product (**1**) (R_f = 0.19) was isolated by column chromatography in silica gel, using toluene as eluent: blue powder, 12 mg (16%); ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$): δ(ppm) = 10.20-9.40 (m, 2H, H-15, H-33), 6.4-5.6 (m, 2H, H-38), 5.50-3.50 (m, 6H, H-40, H-41, H-42), 2.80-2.10 (m, 6H, H-45); Protons 43 and 44 could not be identified; ^{19}F-NMR (470 MHz, $CDCl_3$): δ(ppm) = -137.6 (m, 8F, F-1, F-4, F-8, F-11, F-19, F-22, F-26, F-29), -148.7 (m, 8F, F-2, F-3, F-9, F-10, F-20, F-21, F-27, F-28); FT-IR (KBr), $\bar{\nu}$ (cm^{-1}): 2923, 2852, 1635, 1483 (C-N), 1098; UV-Vis ($CHCl_3$): λ_{max}(nm) (log ε (dm^{3}mol^{-1}cm^{-1})): 694 (5.0), 659 (4.6), 634 (4.6), 606 (4.7), 590 (sh), 491 (4.2), 310 (4.9), 269 (5.1); MALDI-TOF (dithranol): *m/z* = 2017 [M]$^+$, 1296 [M-C_{60}]$^+$; HRMALDI calcd for $C_{120}H_{22}B_2N_{14}O_2F_{16}$: [M$^+$]: *m/z*: 2016.198079, found 2016.194500; elemental analysis calcd (%) for $C_{120}H_{22}B_2N_{14}O_2F_{16}$: C 71.45, H 1.10, N 9.72; found C 72.22, H 1.03, N 9.32.

^{1}H NMR ($C_2D_2Cl_4$, 500 MHz)




373K
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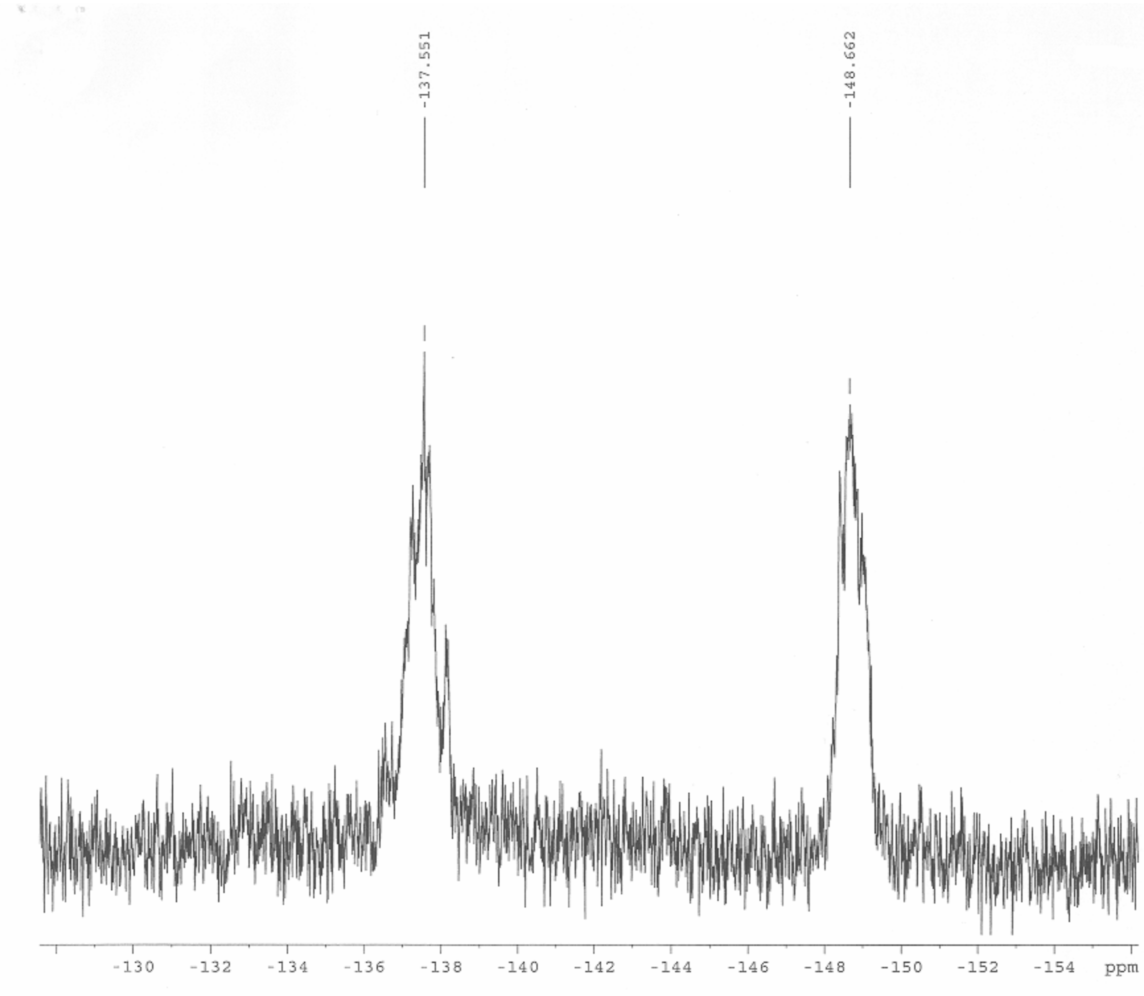
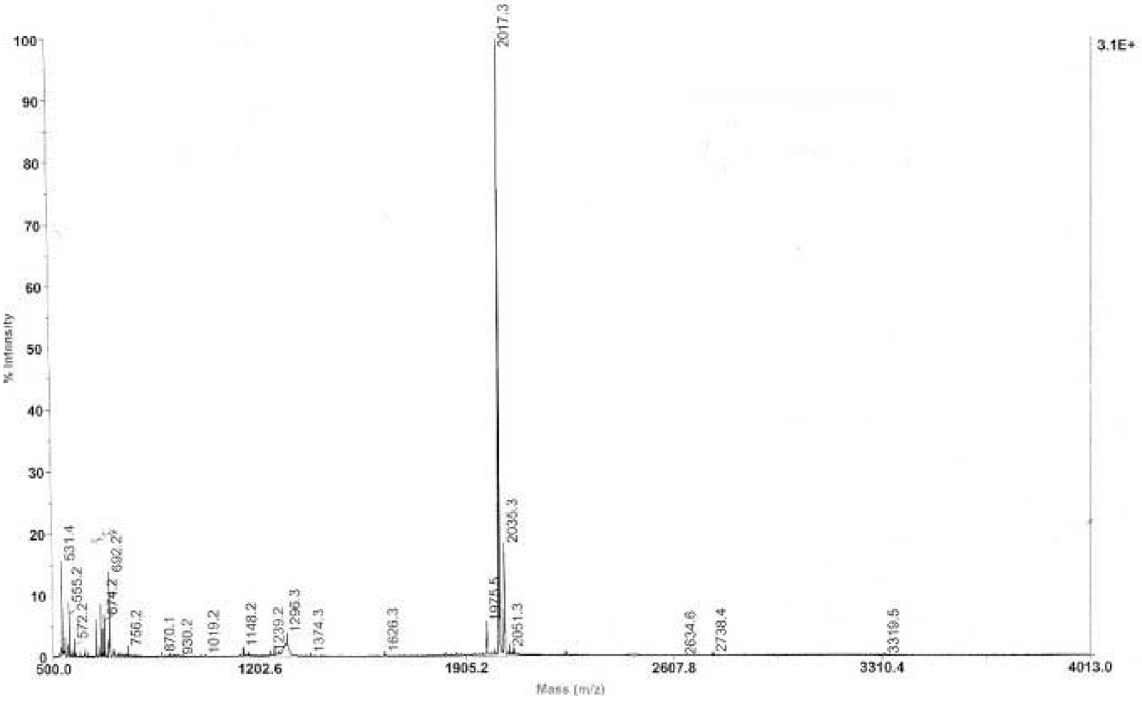
323K
298K
273K
253K
238K
6.0
5.5
5.0
4.5
4.0
3.5
ppm
373K
348K
323K
298K
273K
253K
238K
2.5
2.0

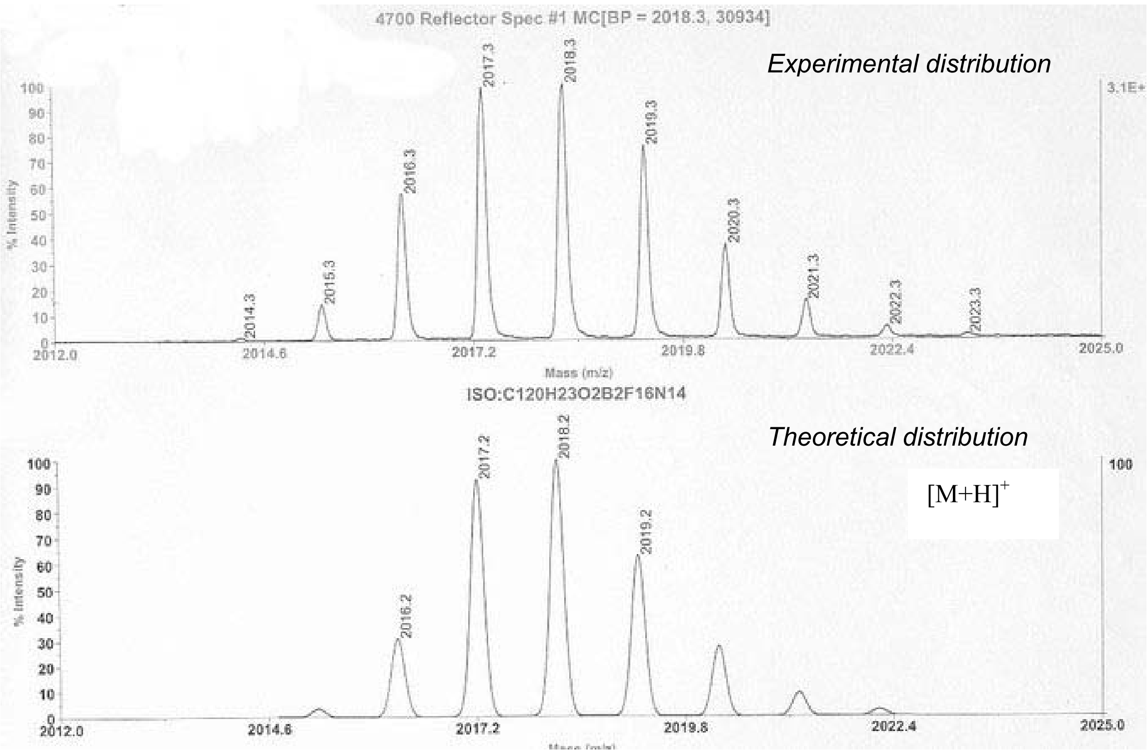
^{19}F NMR (CDCl3, 470 MHz)



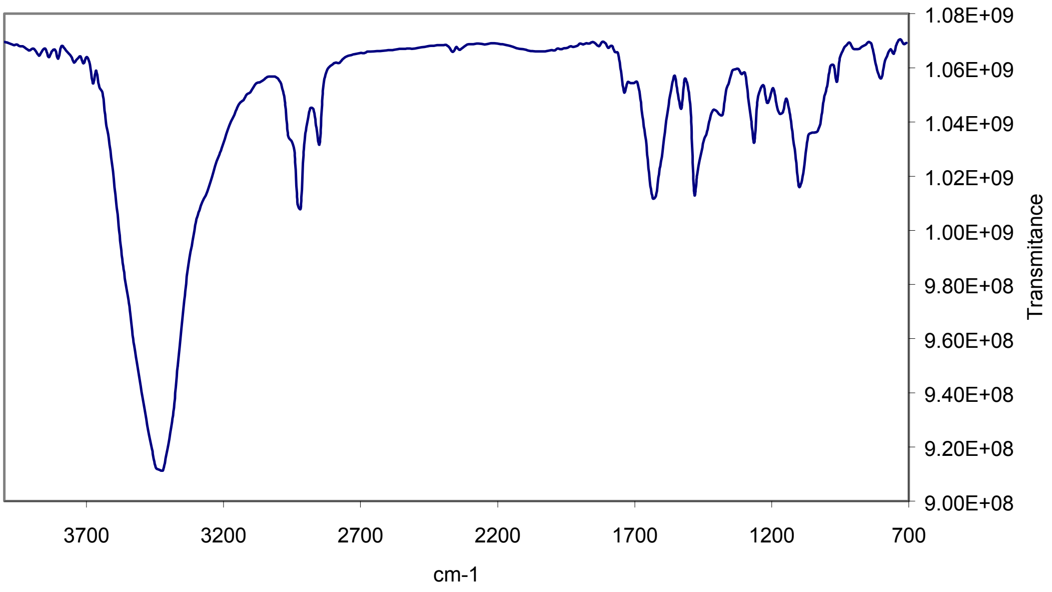
MALDI-TOF (dithranol)



HRMALDI (Isotopic pattern)



FT-IR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1.06E+09
1.04E+09
1.02E+09
1.00E+09
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9.60E+08
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Transmitance
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cm-1

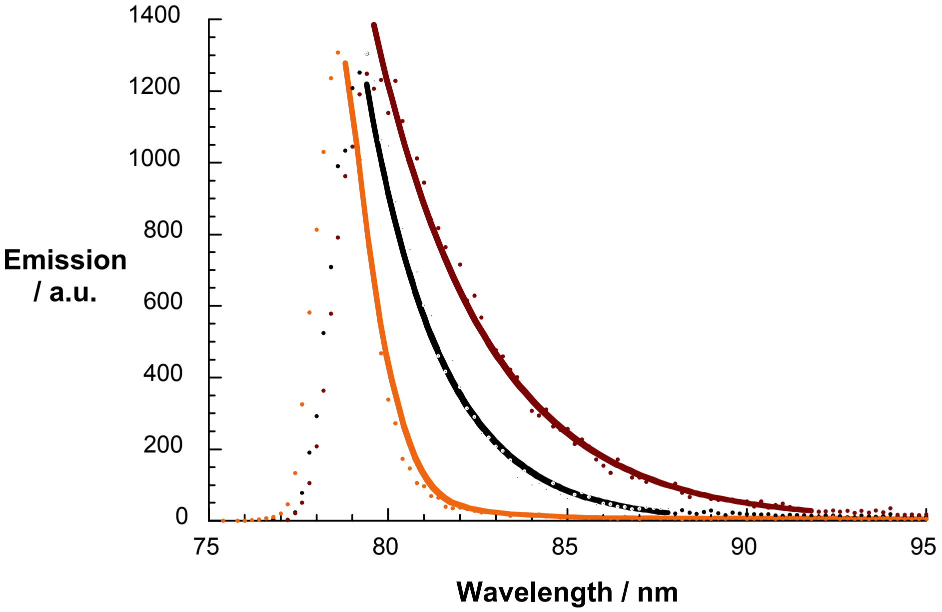

Figure S1: Time resolved fluorescence decay of **2a** (red line), **1** (black line), and laser scatterer (orange line) in room temperature solutions (5×10^{-6} M) – 337 nm excitation wavelength and 710 nm monitoring wavelength.

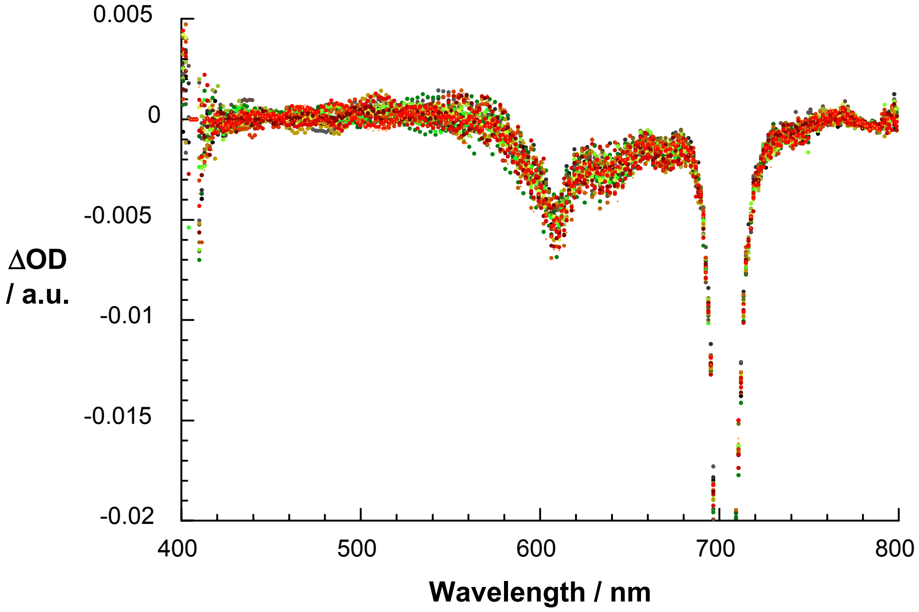

Figure S2. Differential absorption spectrum (visible) obtained upon femtosecond flash photolysis (391 nm) of ~1.0 × 10^{-5} M solutions of **2a** in nitrogen saturated toluene with a several time delay between 0 and 4 ps at room temperature. The spectrum corresponds to the changes that are associated with the formation of the SubPc dimer singlet excited state.

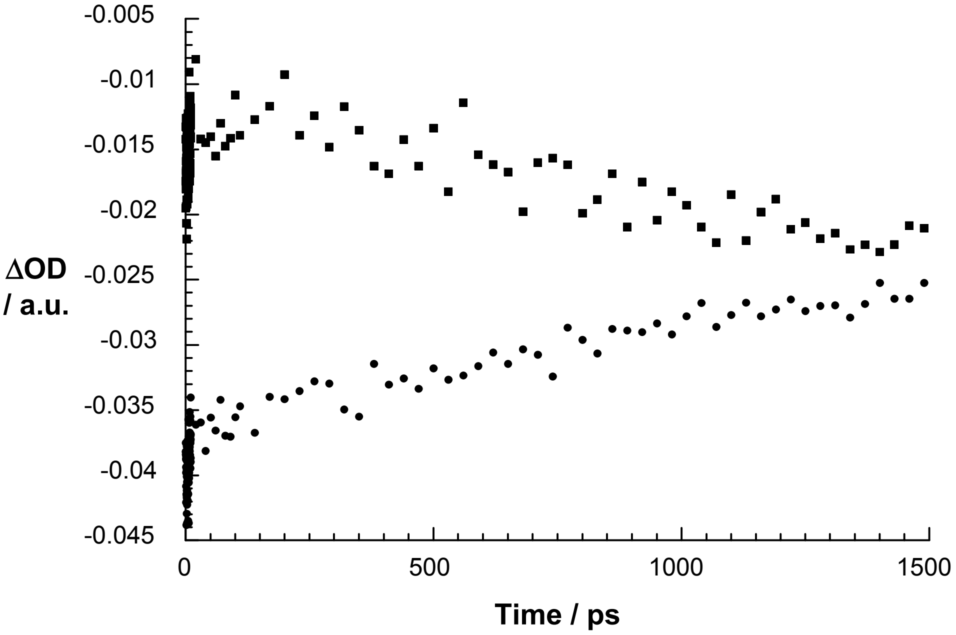

Figure S3: Time-absorption profiles of the SubPc dimer singlet excited state recorded at 700 nm for **2a** (circles) – corresponding to the spectra shown Figure 3 – and for **1** (squares).