

Photoisomerization and Optical Properties of Subphthalocyanine-azobenzene-subphthalocyanine Triad

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1. Experimental details

1.1 X-ray structure determination

Single crystal of **1** was obtained through the slow diffusion of methanol into a chloroform solution. The X-ray crystallographic data for **1** was carried out at 291K on a Rigaku Saturn CCD spectrometer with graphite monochromatized MoK α radiation ($\lambda = 0.71070$ Å). The structure was solved by direct methods and refined on F² by full-matrix least-squares using the Crystal Clear and (SHELXS-97) programs. CCDC 1401329 contains the supplementary crystallography data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; Tel: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

1.2 Synthesis section

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Air and moisture-sensitive reactions were carried out under an argon atmosphere.

Preparation of 4,4'-bis-hydroxyazobenzene **3**¹⁻⁴:

4,4'-bis-hydroxyazobenzene 3: 4-nitrophenol (5 g, 35.9 mmol, 1 eq) and KOH pellets (25 g, 445.6 mmol, 12.4 eq) were dissolved in 10 ml of water and heated at 200 °C for 1 h with mechanical stirring. The reaction mixture turned dark red with vigorous effervescence. The reaction mixture was allowed to cool to room temperature, after which it was dissolved in 50 mL of distilled water to obtain a dark red solution. The mixture was adjusted to pH = 3 by adding conc. HCl, and the product was extracted by washing the solution with diethyl ether and evaporating the ether fraction on a rotary evaporator setup, followed by recrystallization from methanol and water to give a yellow solid (2.23 g, yield: 58%). ¹H NMR (400 MHz, dimethyl sulfoxide-*d*₆) δ 10.11 (s, 2H), 7.72 (d, *J* = 8.8 Hz, 4H), 6.92 (d, *J* = 8.8 Hz, 4H).

Preparation of boron subphthalocyanine chloride **2**⁵:

Boron subphthalocyanine chloride: In a 50 ml two-neck round bottom flask, 2 ml of 1.0 M solution of BCl₃ (234 mg, 2 mmol, 1 eq) in dichloromethane was added to a solution of phthalonitrile (256 mg, 2 mmol, 1 eq) in *p*-xylene (15 ml). The mixture was heated to remove the dichloromethane through distillation using a Dean–Stark condenser. After distillation the flask was heated at reflux (138.5 °C) for 3 h under argon. The products were then cooled and the solvent was removed under reduced pressure. The resultant solid was thoroughly washed with methanol until the filtrate became colorless (158 mg, yield: 55%). ¹H NMR (400 MHz, CDCl₃) δ 8.90–8.93 (m, 6H), 7.95–7.97 (m, 6H). MALDI-TOF-MS *m/z*: calcd for C₂₄H₁₂BClN₆: 430.091, found: 429.912 [M]⁺, 395.067 [M–Cl]⁺.

2. Supplementary data

2.1

Table S1. Crystallography data for **1**.

Parameters name	Data	Parameters name	Data
Empirical formula	C ₆₀ H ₃₂ B ₂ N ₁₄ O ₂	Density (calc.) (Mg/cm ³)	1.13204
Formula weight	1002.62	Absorption coefficient (mm ⁻¹)	0.072
Crystal size (mm ³)	0.27 × 0.25 × 0.22 mm	T (K)	296(2)
Crystal system	Triclinic	F(000)	516
Space group	<i>P</i> -1	Max. and min. transmission	0.9843 and 0.9808
Z	1	Trange for data collection (°)	1.99–25.01
a/Å	10.671(3)	Measured reflections (R(int))	10648 / 5145 [R(int) = 0.1014]
b/Å	11.787(3)	Refinement method	Full-matrix least-squares on F ²
c/Å	12.167(3)	Parameters refined	5145 / 2 / 256
α (deg)	90.260(4)	R indices (all data)	R ₁ = 0.2085, wR ₂ = 0.2973
β (deg)	94.290(5)	Goodness-of-fit on F ²	1.003
γ (deg)	105.427(4)	Largest diff. peak and hole/(eÅ ⁻³)	0.431–0.374
V / Å ³	1470.6(7)		

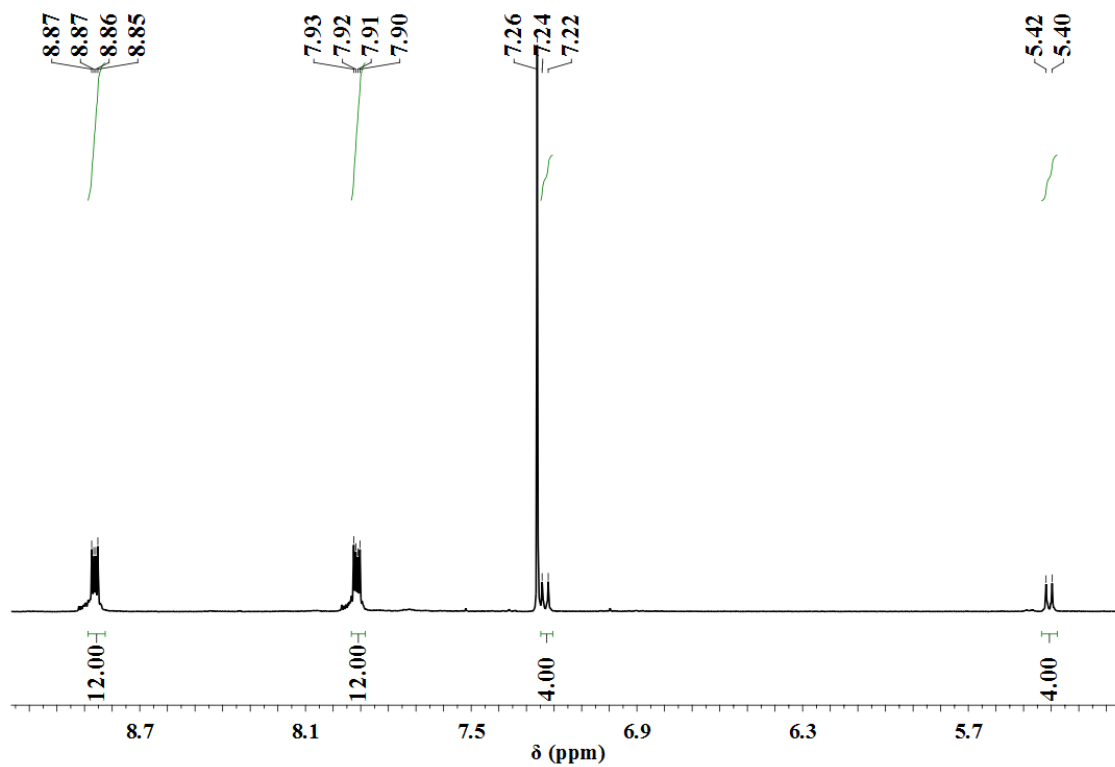


Figure S1. ¹H NMR spectrum of **1** in CDCl₃ (298 K).

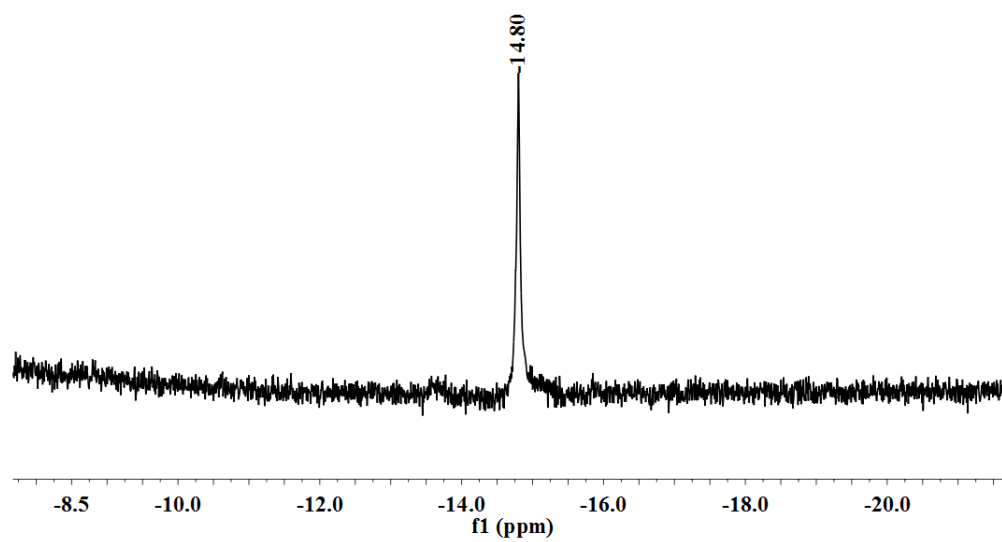


Figure S2. ¹¹B NMR spectrum of **1** in CDCl₃ (298 K).

2.3

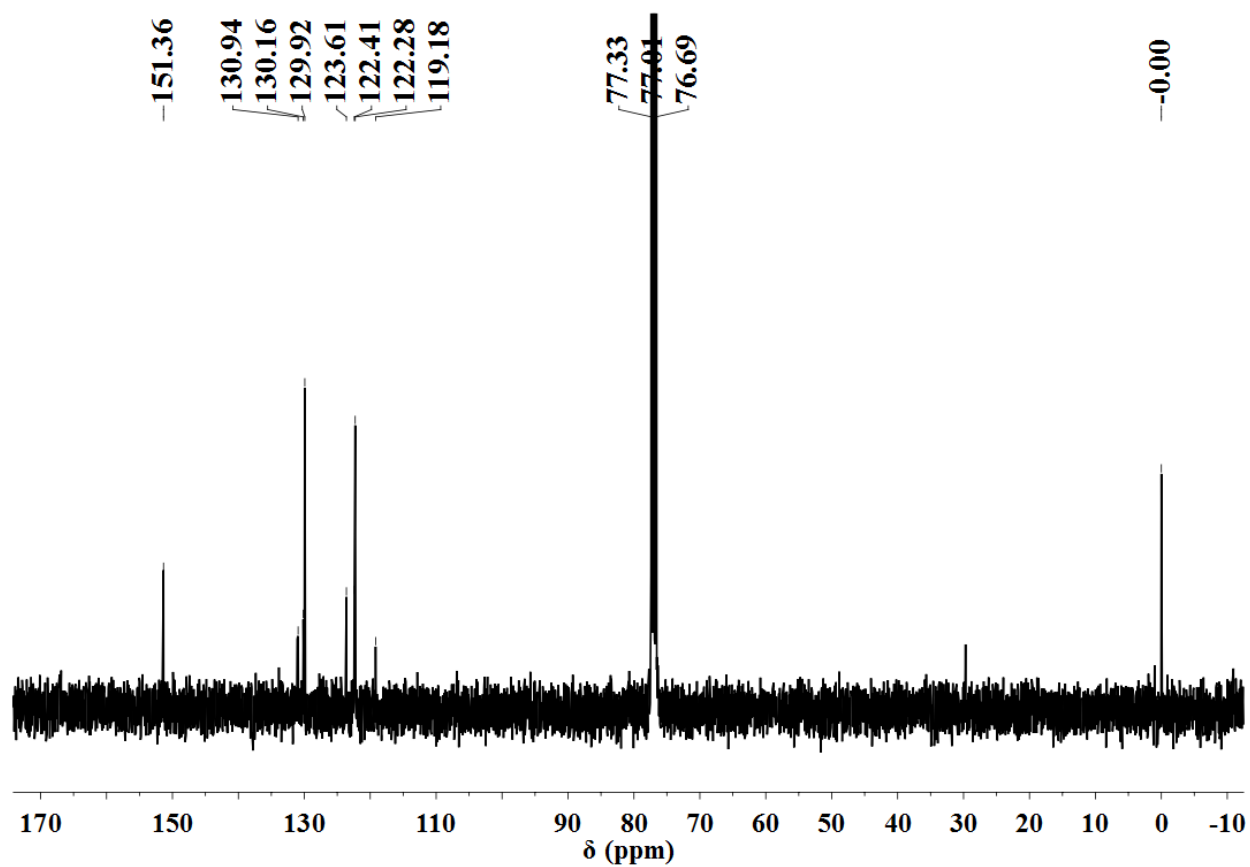


Figure S3. ^{13}C NMR spectrum of **1** in CDCl_3 (298 K).

2.4

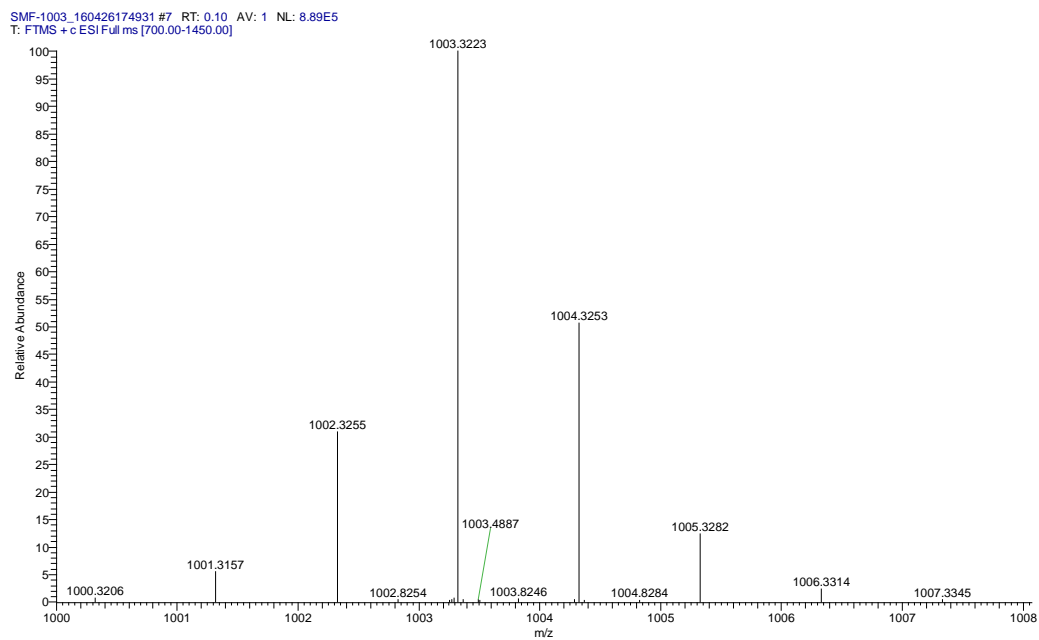


Figure S4. HR-MS data for **1**.

2.5

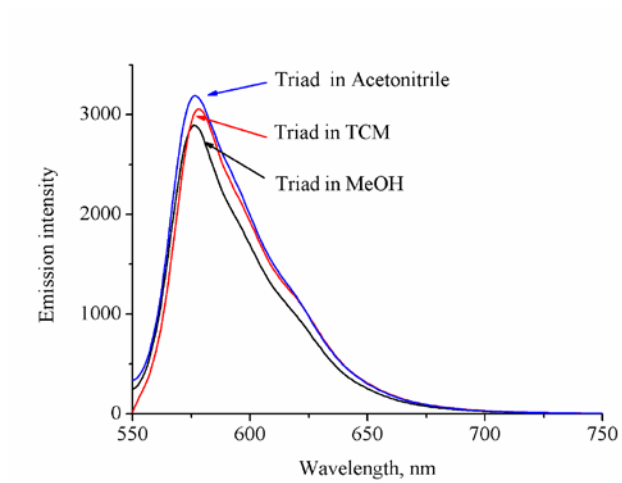


Figure S5. Fluorescence spectra of **1** in different solvents.

2.6

Table S2. Fluorescence lifetime data of **1** in different solvents.

	Lifetime / ns
chloroform	0.94
methanol	1.02
acetonitrile	0.95

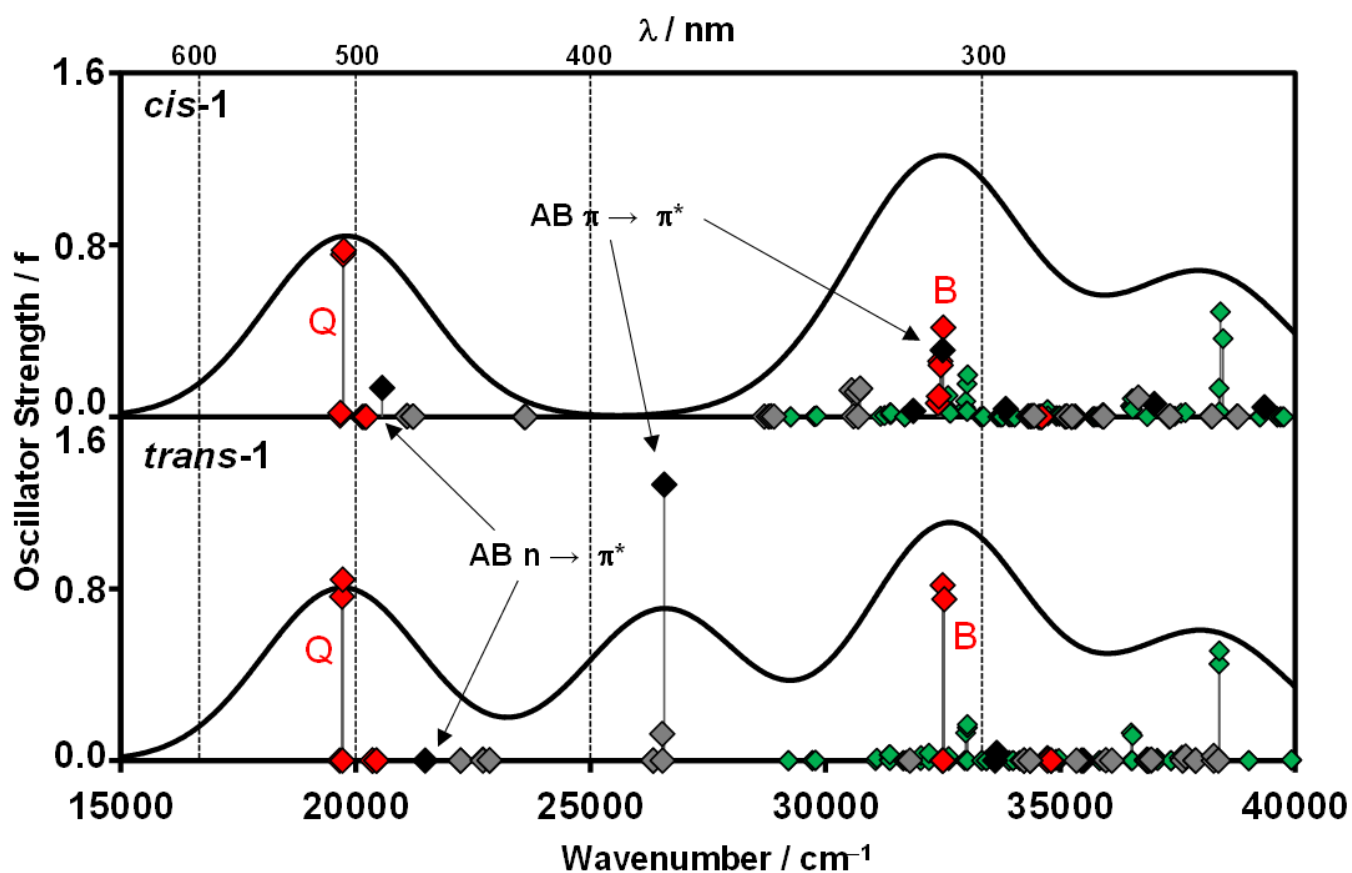


Figure S6. TD-DFT calculations for the B3LYP optimized geometries of *trans-1* and *cis-1* carried out at the B3LYP/6-31G(d) level of theory. The Q and B bands of the subPc moieties are highlighted with red diamonds, while green and black diamonds are used for bands associated with the subPc rings and AB linker, respectively. Gray diamonds denote charge transfer bands. The Chemcraft program was used to generate simulated spectra with a band width at half height of 4000 cm⁻¹.^[6]

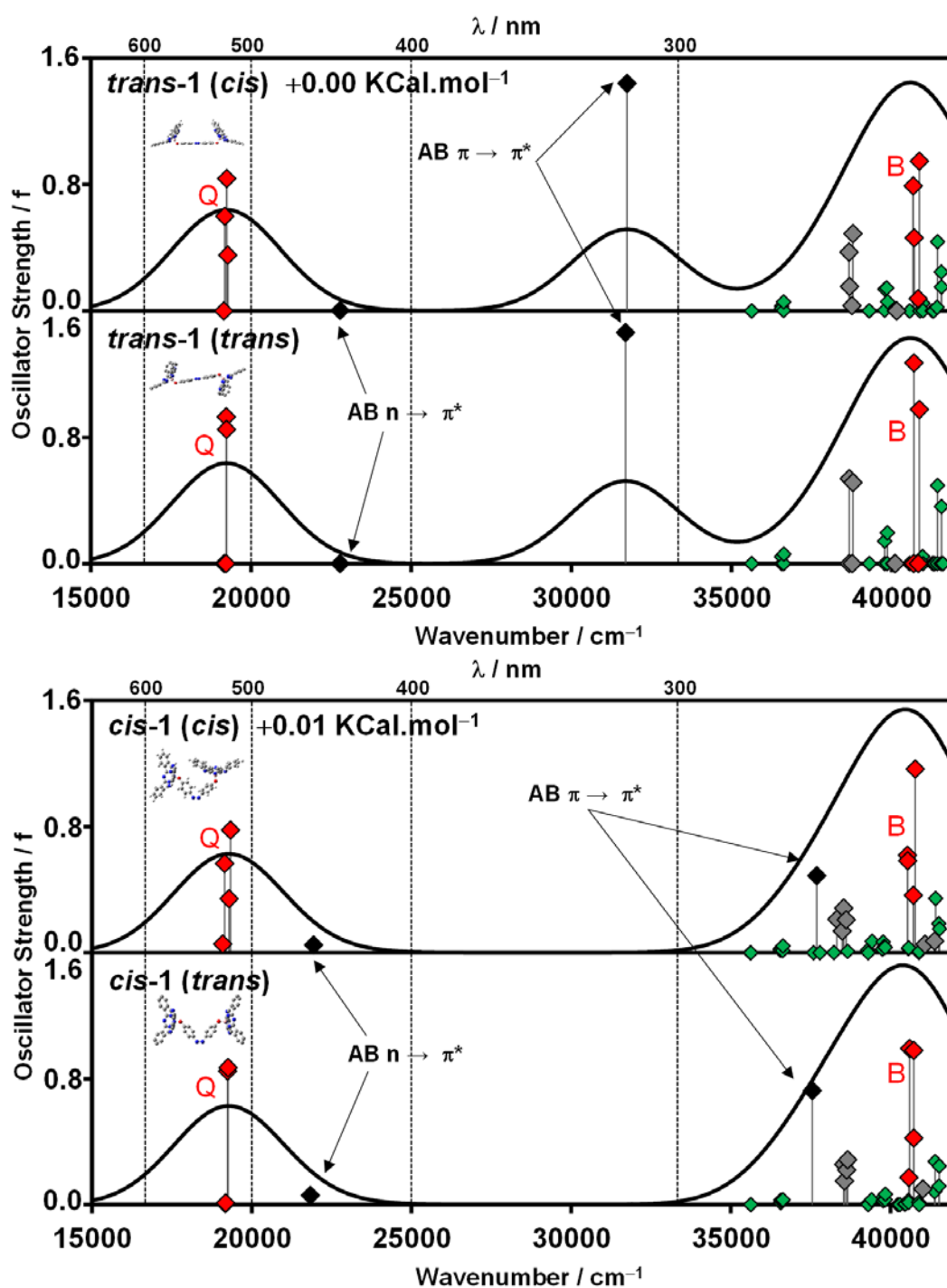


Figure S7. TD-DFT calculations for B3LYP optimized geometries of *trans-1* and *cis-1* carried out at the LC- ω PBE/6-31G(d) level of theory, at minima which differ with respect to the orientation of the subPc rings in a *cis* and *trans* manner with respect to the B–O bonds (as shown in the inset structures). The Q and B bands of the subPc moieties are highlighted with red diamonds, while green and black diamonds are used for bands associated with the subPc rings and AB linker, respectively. Gray diamonds denote charge transfer bands. The Chemcraft program was used to generate simulated spectra with a band width at half height of 4000 cm^{-1} .^[6]

References:

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