Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Supporting Information

Rosindone Revisited: A Computational and Photophysical Study of 7-Phenylbenzo[a]phenazine-5(7H)-one (PBP)

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Contents

S11. Corrected phosphorescence spectrum recorded for **PBP** in an ethanol glass at 80K.

S12. The change in fluorescence with decreasing temperature for a solution of **PBP** in ethanol. Insert show the plot for calculation of the activation energy using the Arrhenius expression.

S13. Excitation spectrum (black) and emission spectrum (red) recorded for **PBP** in an ethanol glass at 80K.

S14. ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **PBP**.

S15. ^{13}C NMR (175 MHz, $CDCl_3$) spectrum of **PBP**.

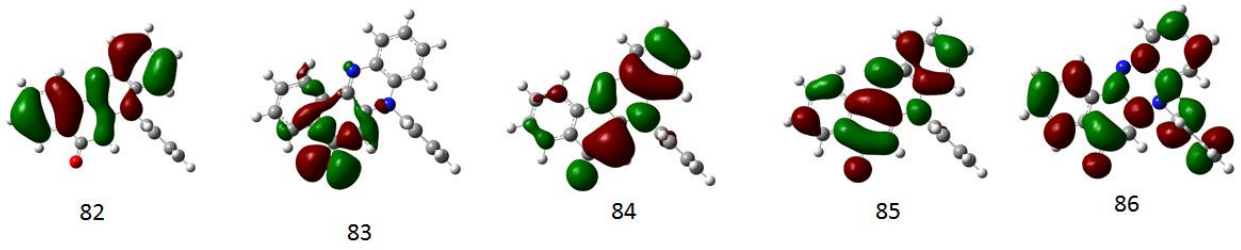
Table S1. DFT calculated dipole moments and wavelength maximum values for **PBP** in a selection of solvents with different polarity.

Solvent	**Dipole Moment / D**	**λ_{max} / nm**[b,c]	**Molecular Orbitals**[d,e]
Gas-phase	5.55	463 (0.187)	82-85 (0.017) 84-85 (0.462) 84-86 (0.011)
MeCN	8.95	475 (0.281)	83-85 (0.012) 84-85 (0.473)
CHEX[f]	6.70	475 (0.285)	82-85 (0.011) 84-85 (0.474)
DMSO[g]	9.00	477 (0.296)	83-85 (0.011) 84-85 (0.474)
THF[h]	8.23	476 (0.289)	83-85 (0.011) 84-85 (0.474)
DCM[j]	8.37	477 (0.293)	83-85 (0.011) 84-85 (0.474)
Toluene	6.95	476 (0.298)	84-85 (0.476)
MeOH	8.93	475 (0.277)	83-85 (0.012) 84-85 (0.472)

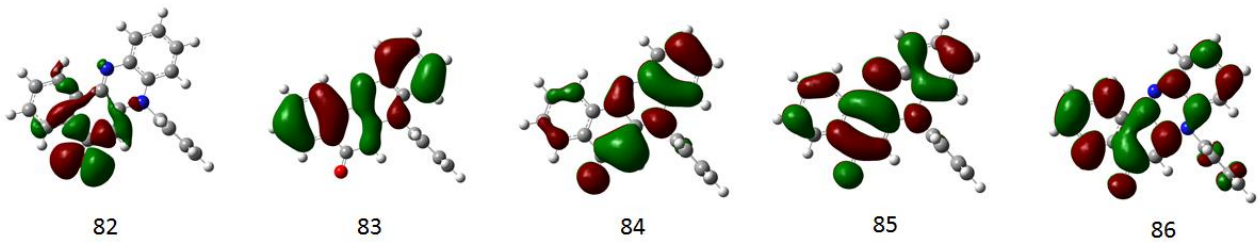
[a] DFT calculated parameters using B3LYP and 6-311G+(d) basis set and IEFPCM in Gaussian 09. [b]Calculated using TD-DFT and IEFPCM in Gaussian 09. [c] Calculated oscillator strength, [d] numbering of molecular orbitals involved in the absorption envelope, [e] square of molecular orbital coefficient, [f]cyclohexane, [g]dimethylsulfoxide, [h]tetrahydrofuran, [j] dichloromethane

Selected Kohn-Sham Frontier Molecular Orbitals

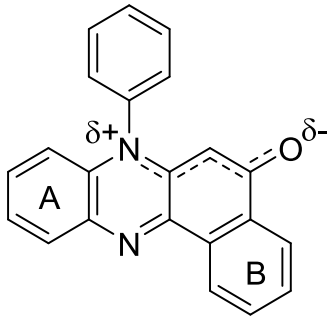
Gas Phase + Cyclohexane

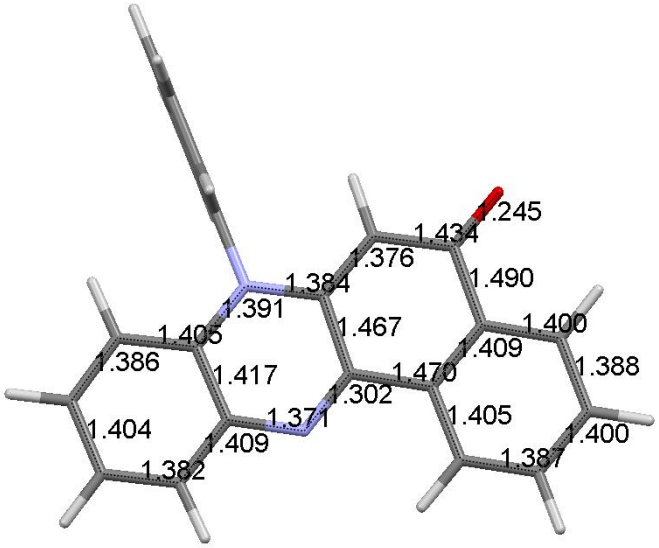


MeCN, Toluene, THF, DCM, MeOH, DMSO

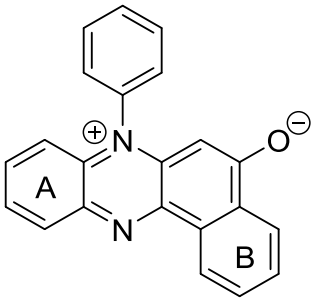


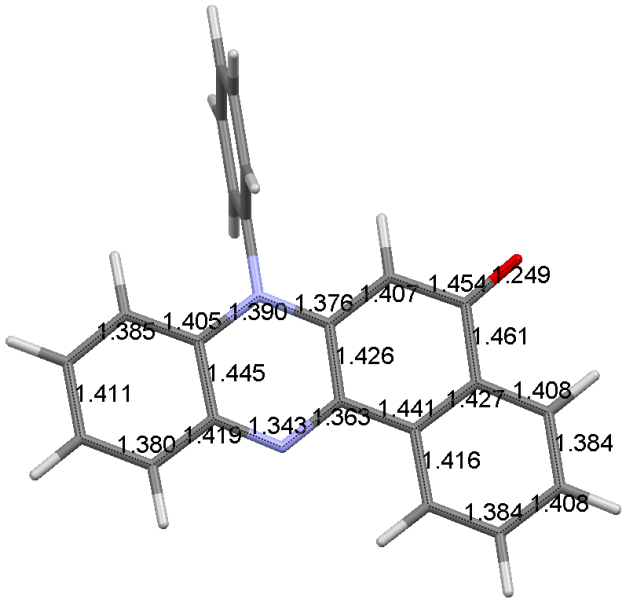
Ground State (Dipole Moment = 8.95D)





First Excited Singlet State (Dipole Moment = 9.71D)

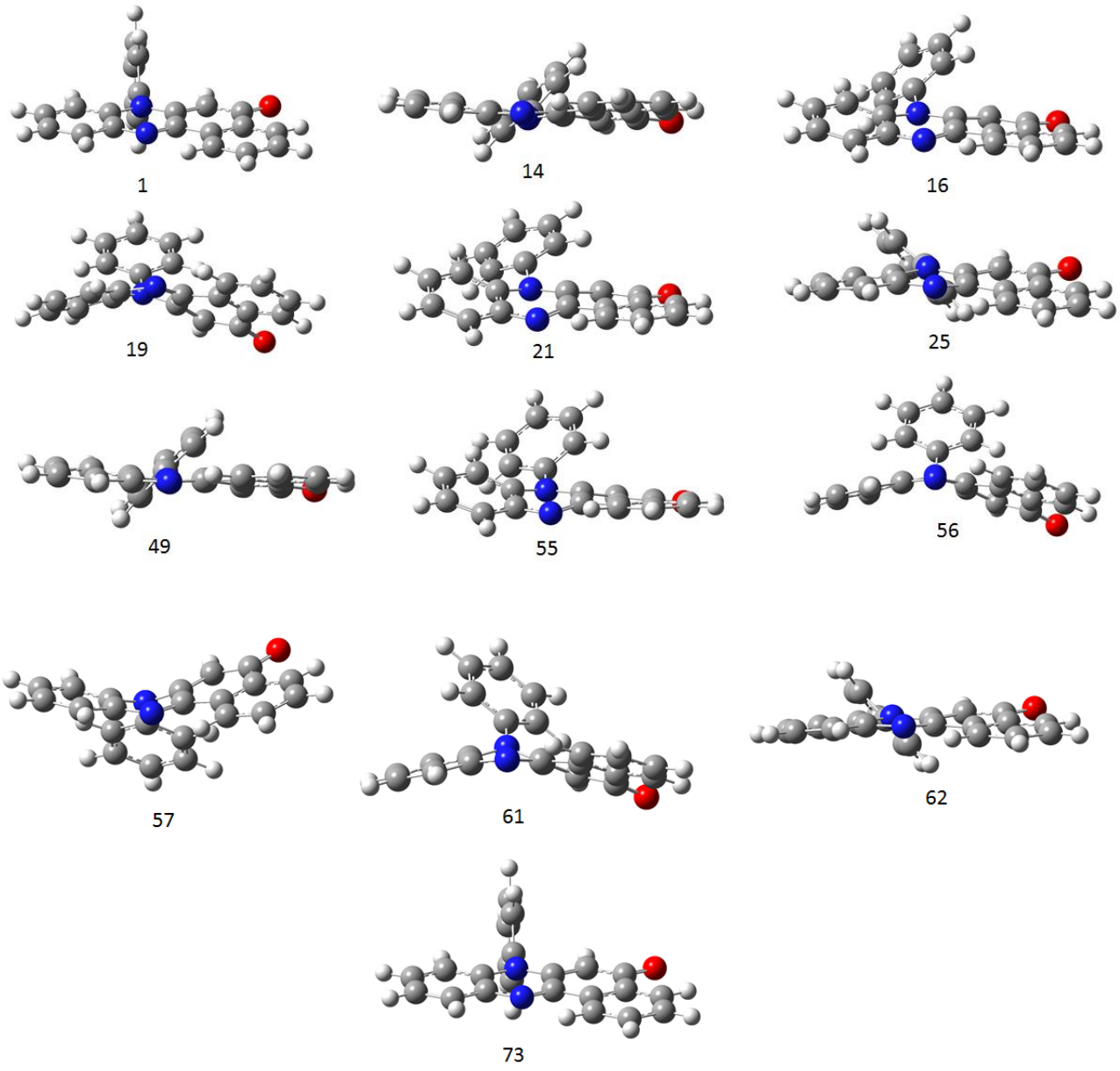




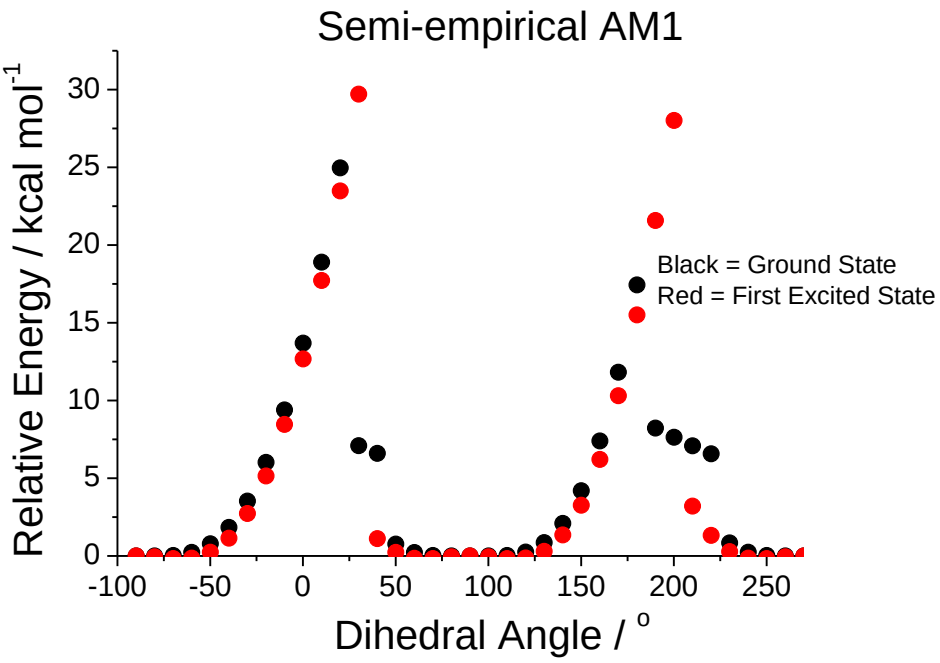
S1. Comparison of TD-DFT calculated bond lengths for the ground and first-excited singlet state structures for **PBP** in a MeCN solvent bath. Note the changes in the bond orders are collected in Table 1.

Table S2. Bond order (NBO) for C-C bonds calculated using Pauling's expression $D = D_1 - 0.70 \log NBO$ and where D is the observed bond length and D_1 is the expected bond length (1.504 Å).

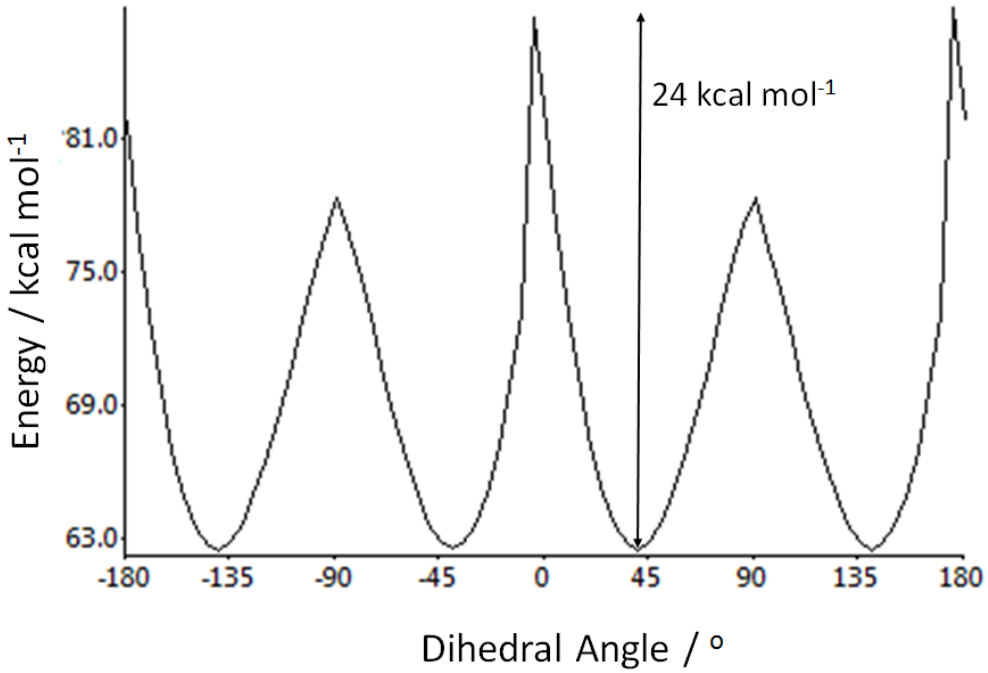
Ground State		Excited State			
D / Å	**N_{BO}**	**D / Å**	**N_{BO}**	**ΔN_{BO}**	**% Change**
1.376	1.52	1.407	1.38	-0.14	*-9.2*
1.434	1.26	1.454	1.18	-0.08	-6.3
1.490	1.05	1.461	1.15	0.1	*9.5*
1.400	1.41	1.408	1.37	-0.04	-2.8
1.388	1.47	1.384	1.48	0.01	0.68
1.400	1.41	1.408	1.37	-0.04	-2.8
1.387	1.47	1.384	1.48	0.01	0.68
1.405	1.39	1.416	1.34	-0.05	-3.6
1.409	1.37	1.427	1.29	-0.08	-5.8
1.470	1.12	1.441	1.23	0.11	*9.8*
1.467	1.13	1.426	1.29	0.16	*14.1*
1.405	1.39	1.405	1.39	0	0
1.386	1.47	1.385	1.48	0.01	0.68
1.404	1.39	1.411	1.36	-0.03	-2.2
1.382	1.49	1.380	1.50	0.01	0.67
1.409	1.37	1.419	1.32	-0.05	-3.6
1.417	1.33	1.445	1.21	-0.12	*-9.0*
				Overall change	-9.19%



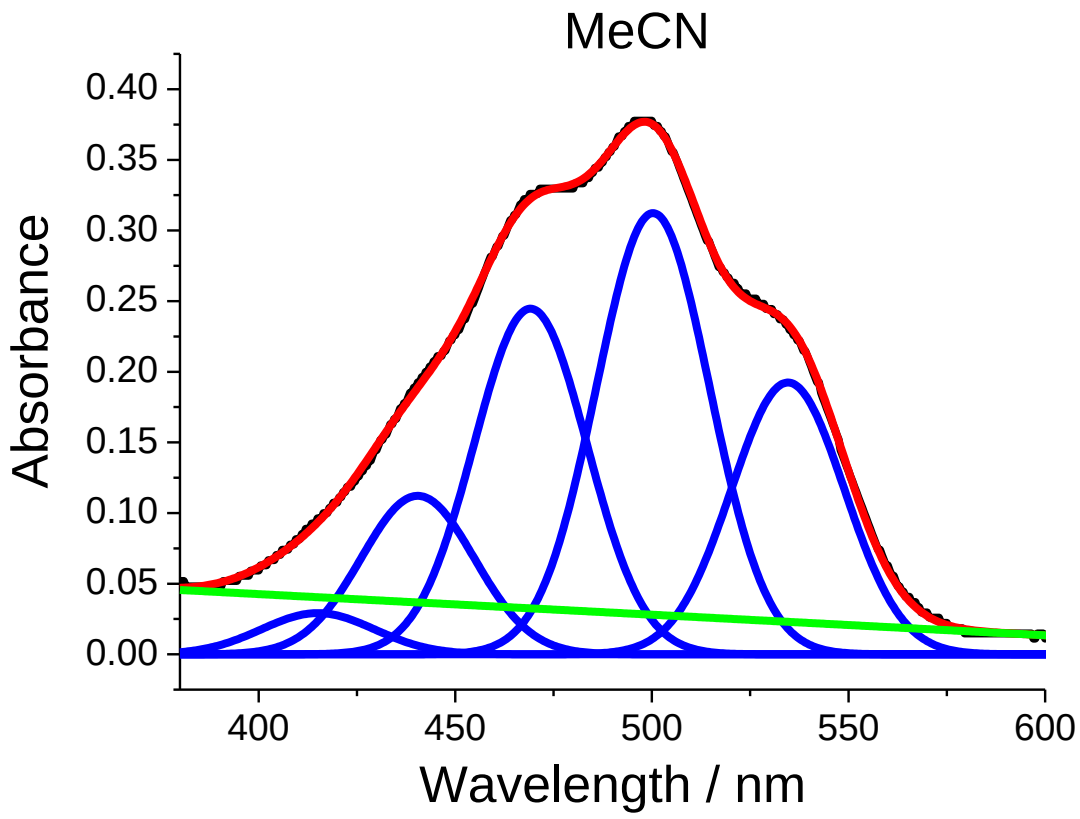
S2. DFT B3LYP, 6-311G+(d) calculated molecular geometries of **PBB** in the gas phase as the phenyl group is rotated through 360^{o} at 5^{o} intervals starting at step 1.



S3. Relative energies of **PBP** in the ground state (black) and first-excited state (red) versus the dihedral angle at the *N*-phenyl subunit calculated using a semi-empirical (AM1) method. Each point represents a change in angle of 10°.



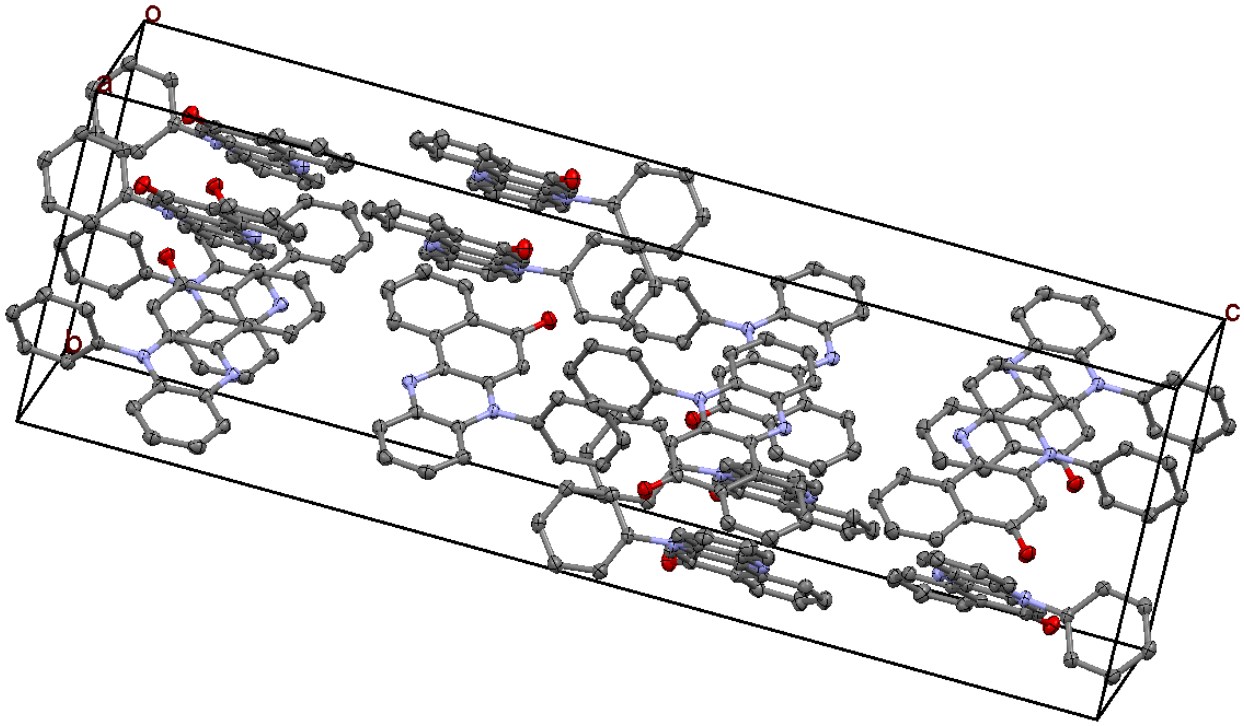
S4. MM^+ single angle calculation results for **PBP** as the phenyl group is rotated using the program Chem3D.



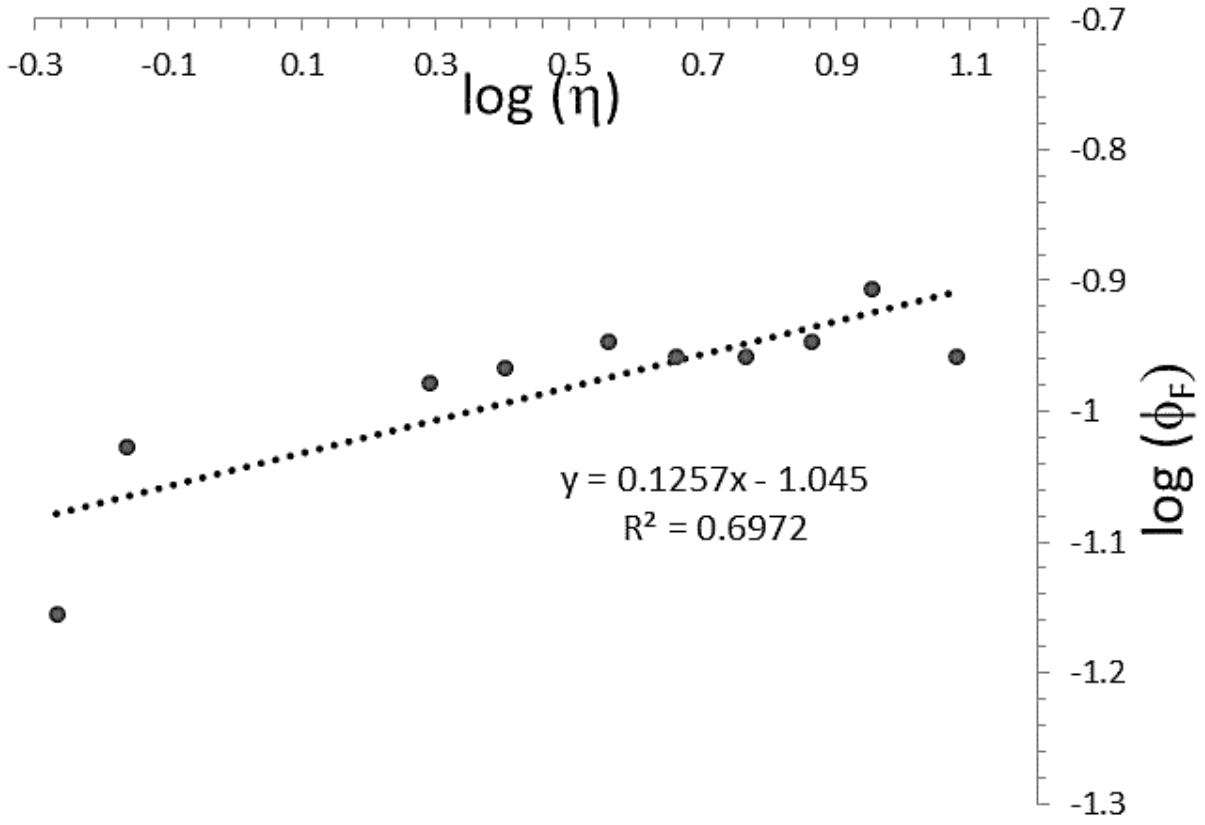
S5. Selected absorption profile for **PBP** showing the actual spectrum (black) and reconstructed spectrum (red) using the constant half-width Gaussian profiles (blue). The green line shows the fitted baseline.

Table S3. Crystal data and structure refinement for **PBP**

Empirical formula	$C_{22}H_{14}N_2O$
Formula weight	322.35
Temperature/K	150.0(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.23403(10)
b/Å	10.88902(13)
c/Å	34.4570(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3089.43(7)
Z	8
ρ_{calc}g/cm^3	1.386
μ/mm^{-1}	0.683
F(000)	1344.0
Crystal size/mm^3	0.21 × 0.12 × 0.06
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.268 to 133.618
Index ranges	$-9 \leq h \leq 6$, $-10 \leq k \leq 12$, $-41 \leq l \leq 39$
Reflections collected	18745
Independent reflections	2720 [R_{int} = 0.0319, R_{sigma} = 0.0176]
Data/restraints/parameters	2720/0/226
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0851
Final R indexes [all data]	R_1 = 0.0411, wR_2 = 0.0905
Largest diff. peak/hole / e Å^{-3}	0.14/-0.22

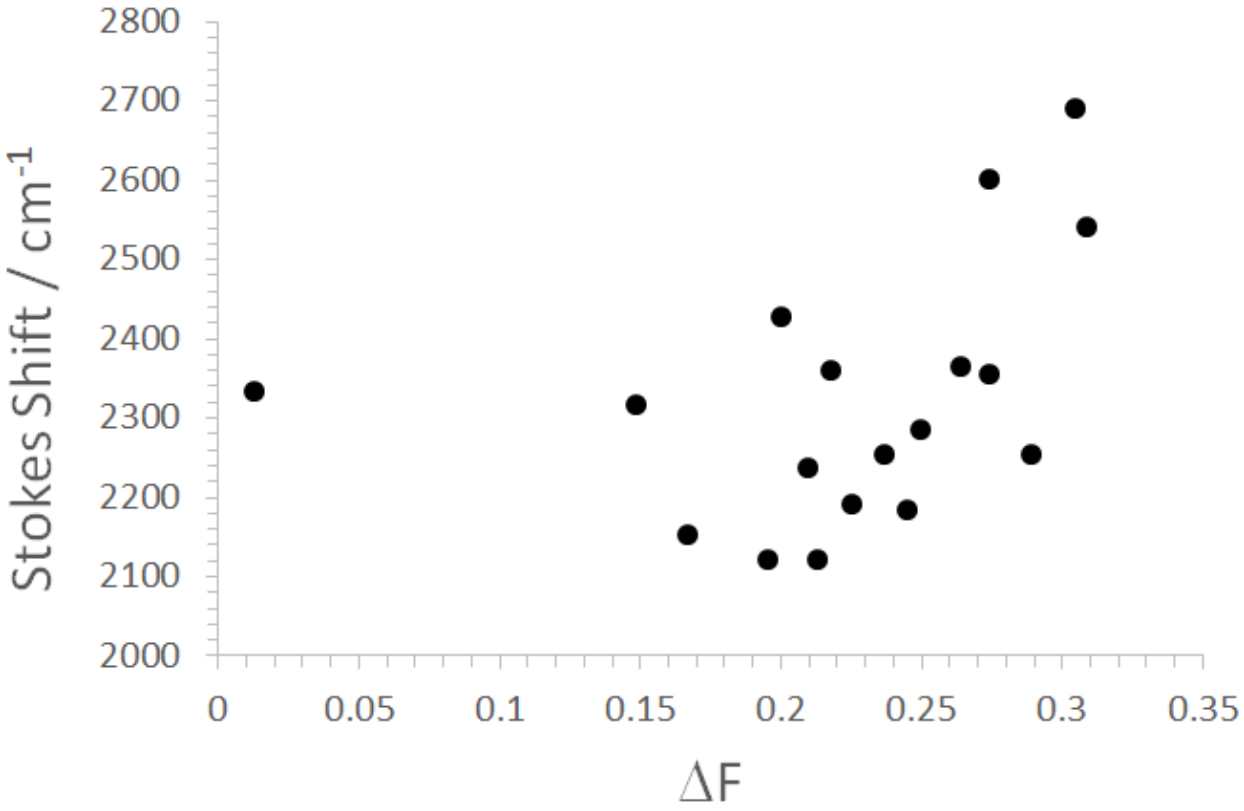


S6. Crystal packing diagram for **PBP**.

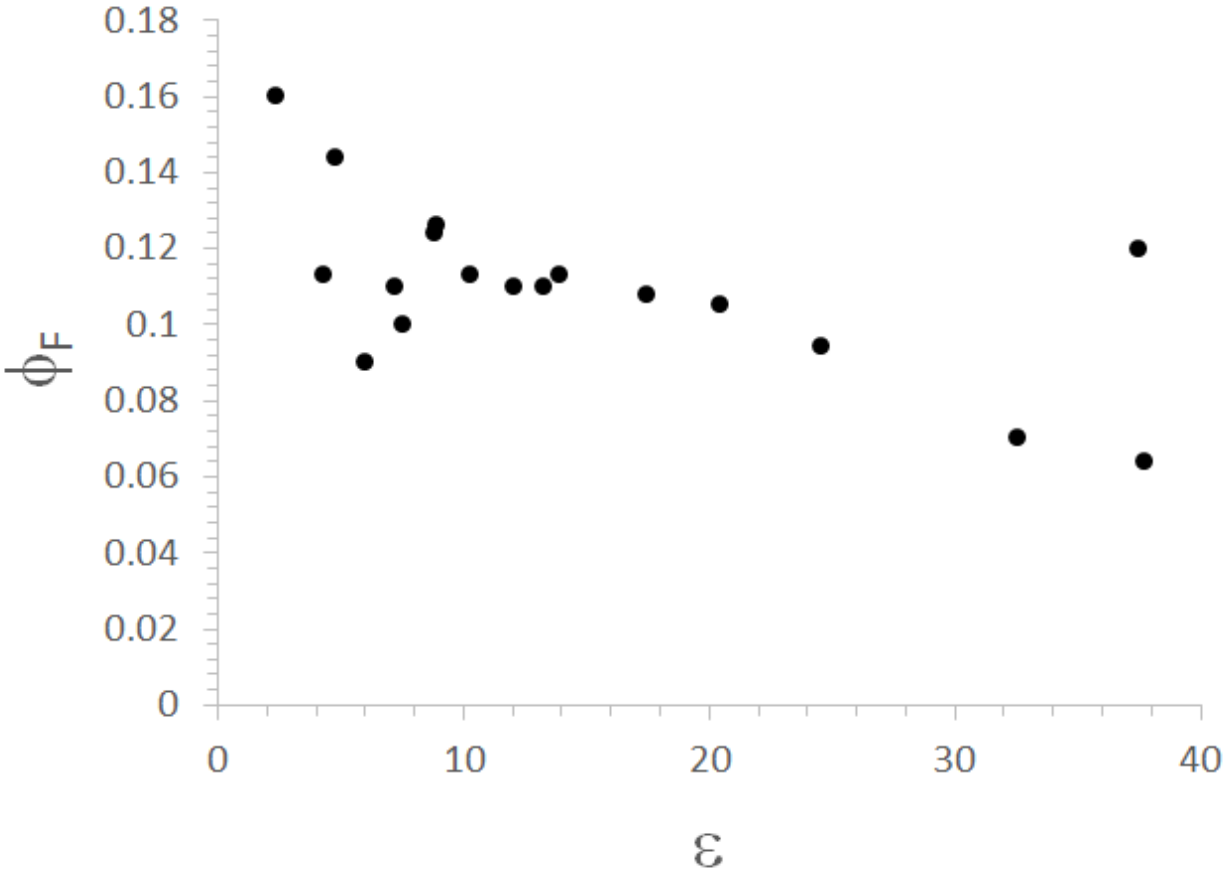


$$\log \phi_{\mathrm{FLU}} = \alpha log\ \eta + \mathrm{C}\ (\mathrm{Eq.}\ 1)$$

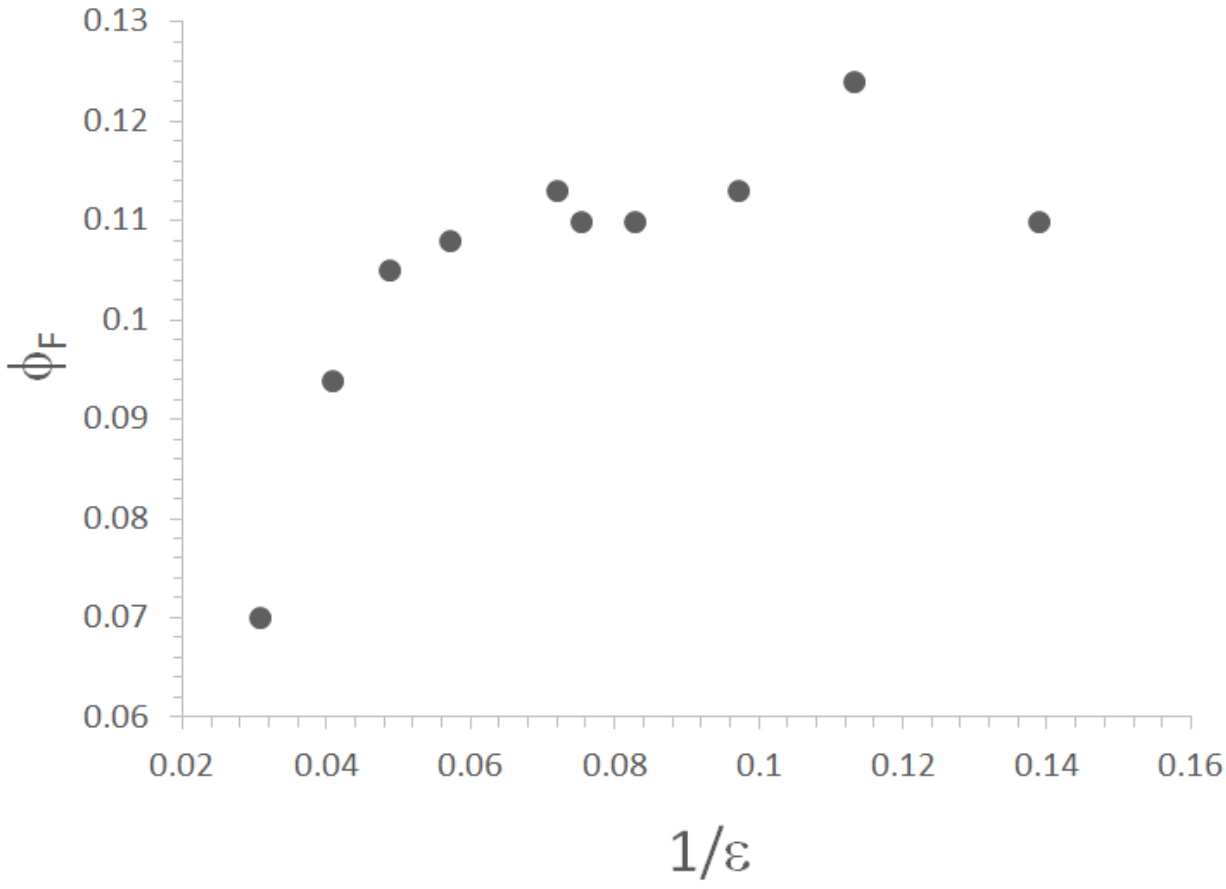
S7. Fit of quantum yields to solvent viscosity using the Forster-Hoffmann equation for the linear mono-protic alkanol solvents. Dashed line depicts least squares fit to the data points and the goodness-of-fit. Insert shows the linear equation and R^2.



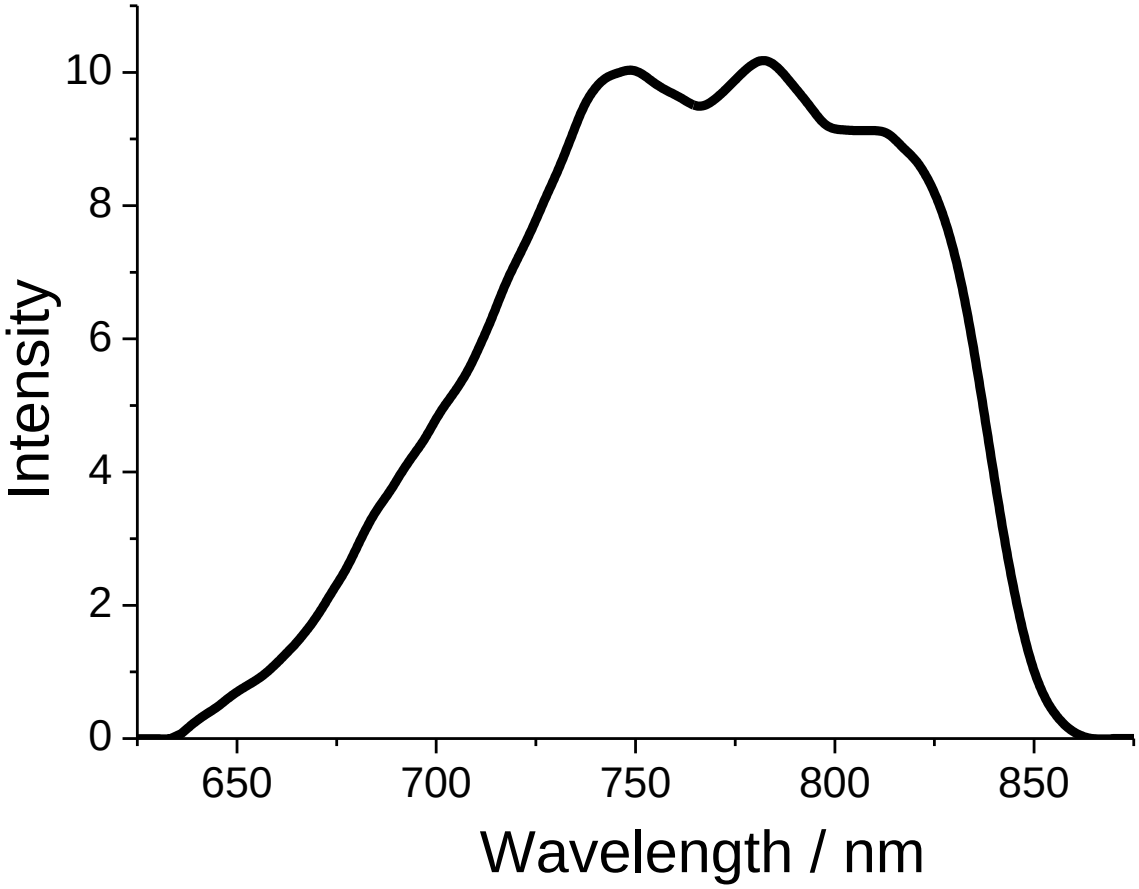
S8. Relationship between Stokes Shift (SS) and the solvent Pekar function ΔF for a range of protic and aprotic solvents.



S9. Variation of the quantum yield of fluorescence (ϕ_F) with the dielectric constant (ε) for a range of protic and aprotic solvents.



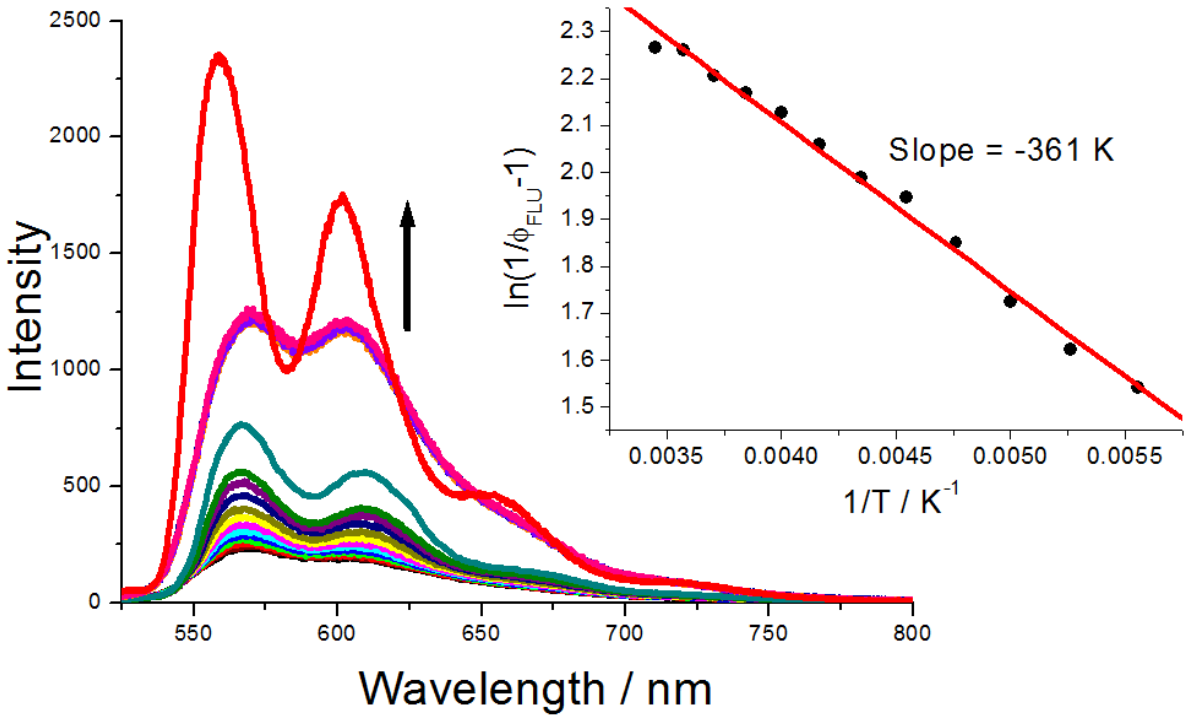
S10. Variation of the quantum yield of fluorescence (ϕ_F) with the reciprocal of the dielectric constant (ε) for a range of linear mono-protic alkanol solvents.



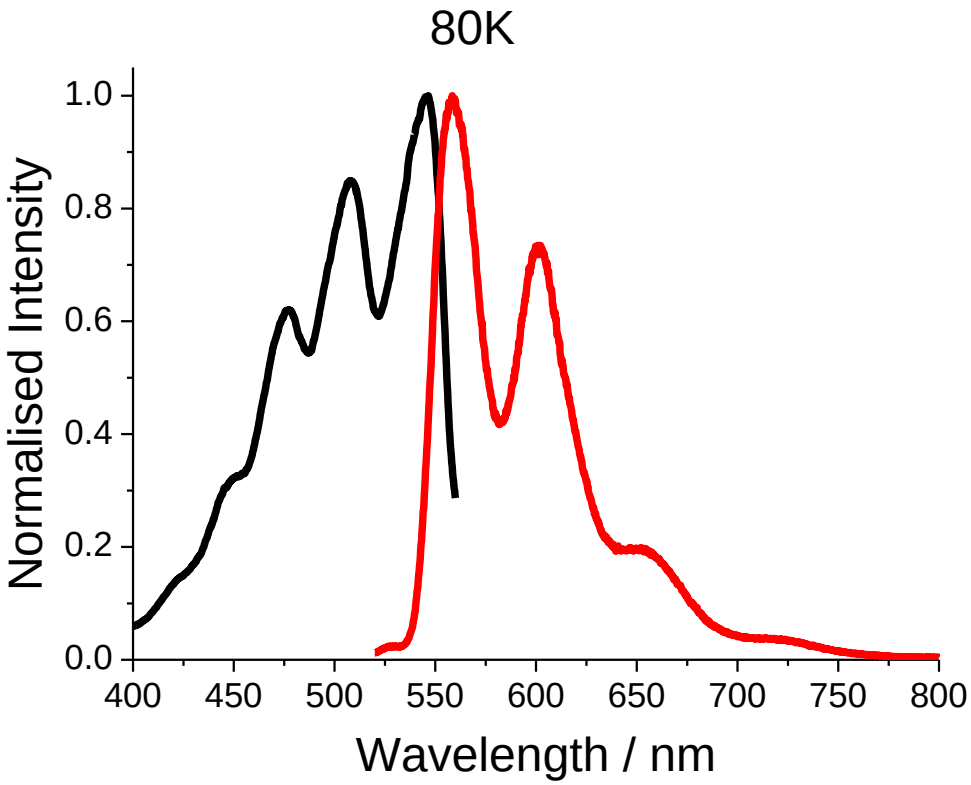
S11. Corrected phosphorescence spectrum recorded for **PBP** in an ethanol glass at 80K.

Given that $k_{NR} = k_{RAD}((1/\phi_{FLU})-1)$ and assuming k_{RAD} remains constant with temperature then a plot of $\ln((1/\phi_{FLU})-1)$ vs 1/T will provide a slope = $-\Delta E/R$.

k_{NR} = non-radiative rate, k_{RAD} = radiative rate, ΔE = activation energy and R = gas constant.



S12. The change in fluorescence with decreasing temperature for a solution of **PBP** in ethanol. Insert show the plot for calculation of the activation energy using the Arrhenius expression.



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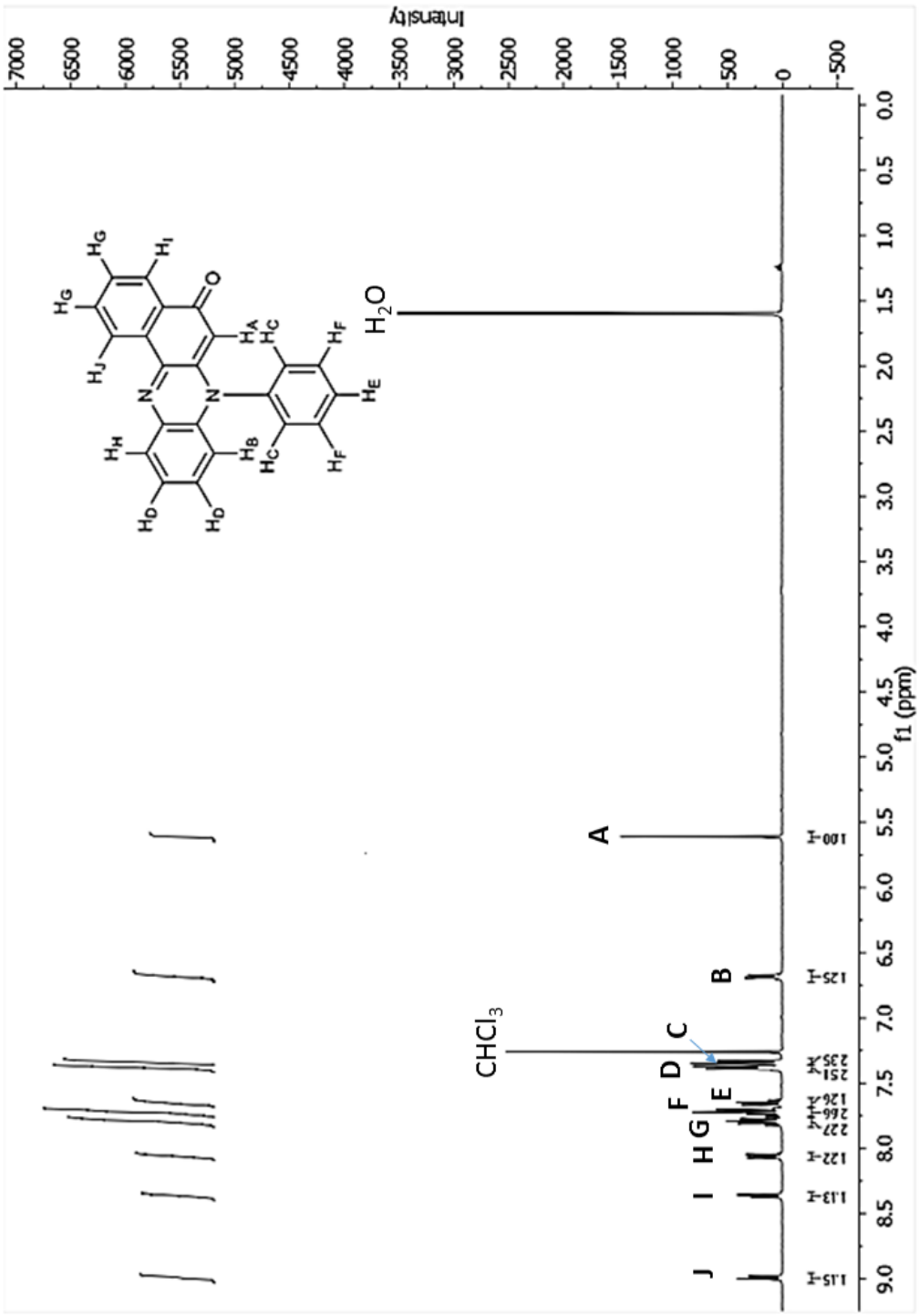
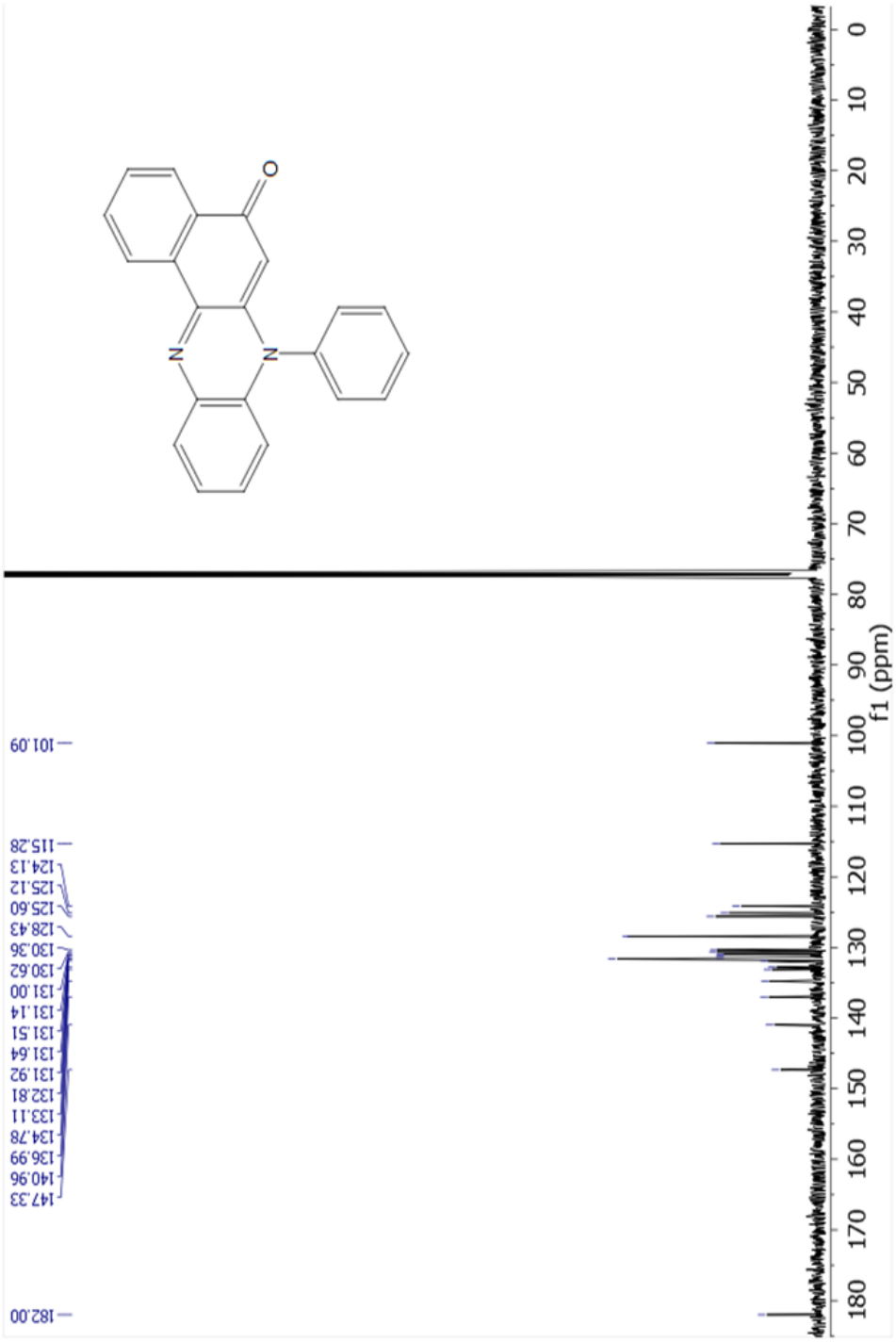


S14. ^{1}H NMR (700 MHz, $CDCl_3$) spectrum of **PBP**.



S15. ^{13}C NMR (175 MHz, $CDCl_3$) spectrum of **PBP**.