Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

A binaphthalimide motif as a chiral scaffold for thermally activated delayed fluorescence with circularly polarized luminescence activity.

Yugo Tsuji[a]‡, Natsuko Kanno[b]‡, Chigusa Goto[a], Shohei Katao[a], Yasuo Okajima[a], Pablo Reine[a], Paulius Imbrasas[c], Sebastian Reineke[c], Katsuyuki Shizu[b], Takuya Nakashima[a], Hironori Kaji[b], Tsuyoshi Kawai[a]*, Marine Louis[a]*.

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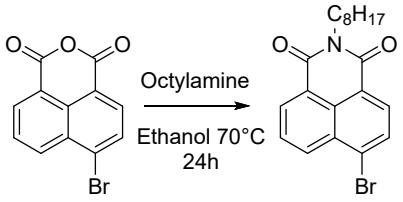
NMR Spectra



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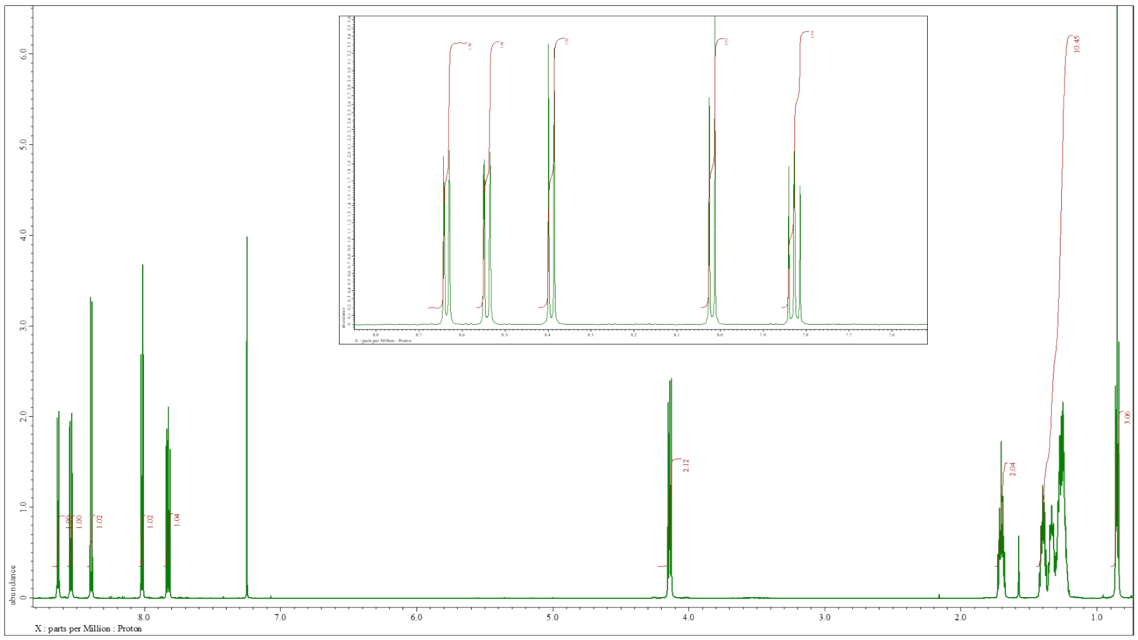

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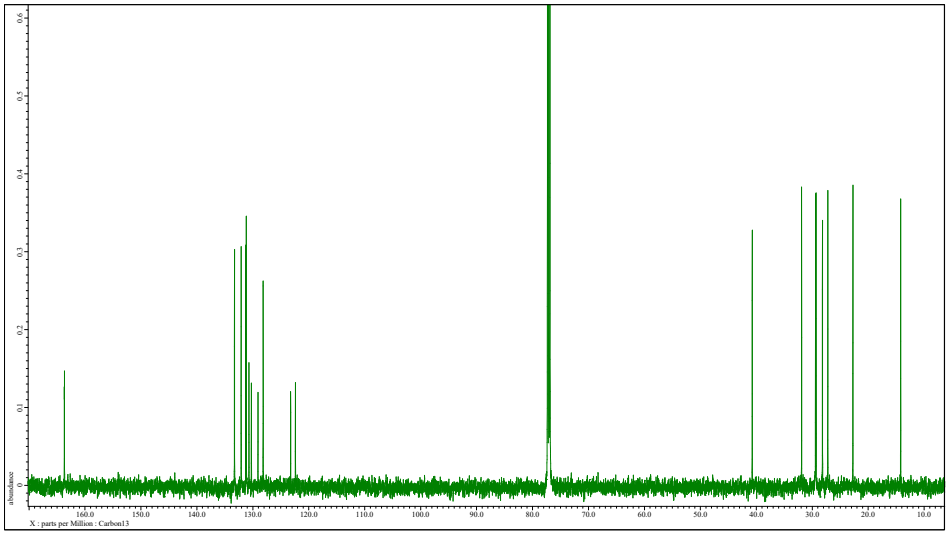

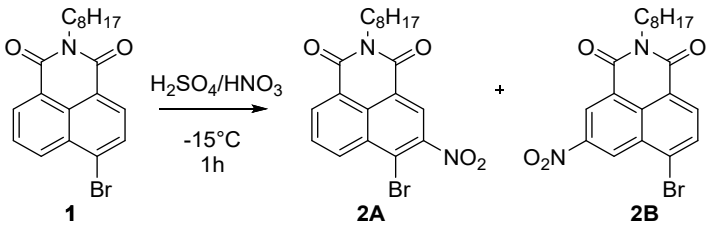

1 **2A** **2B**

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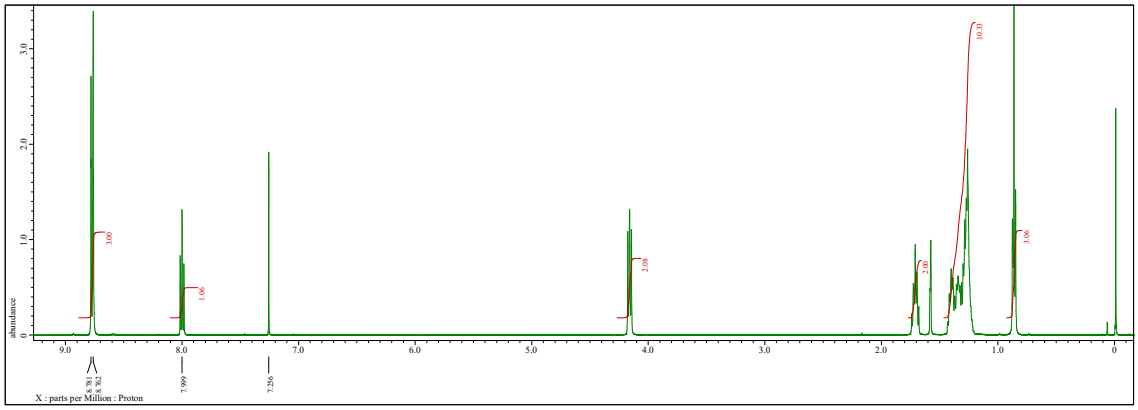

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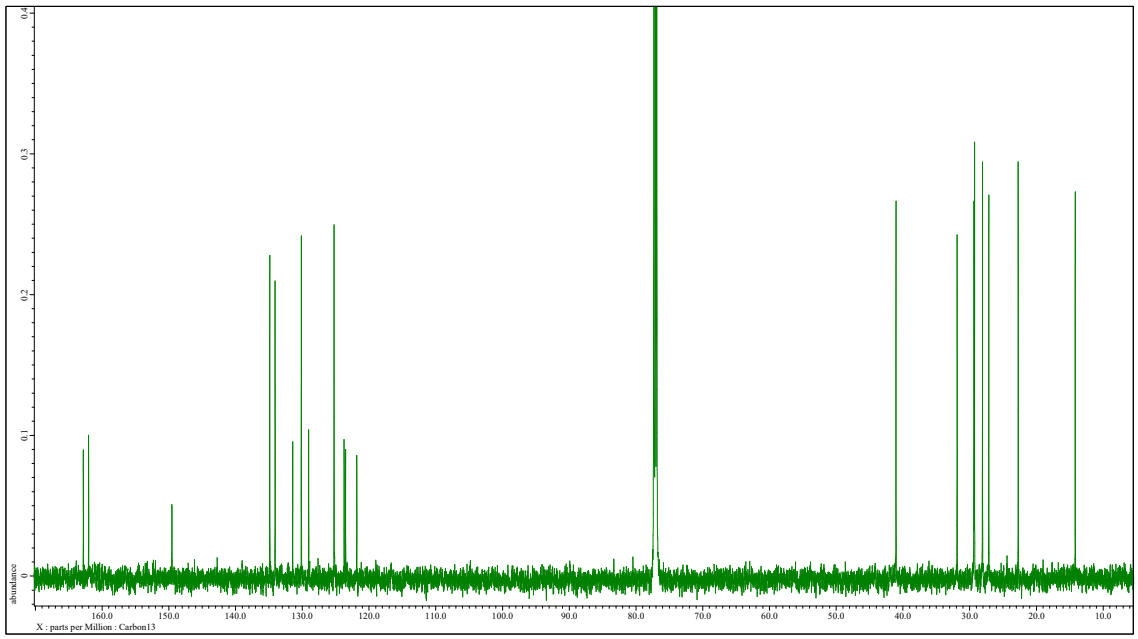

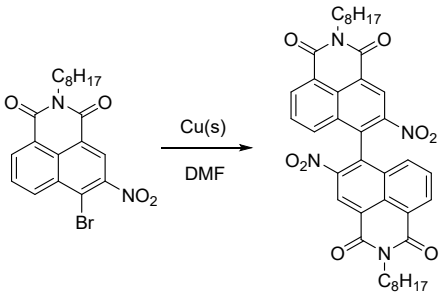

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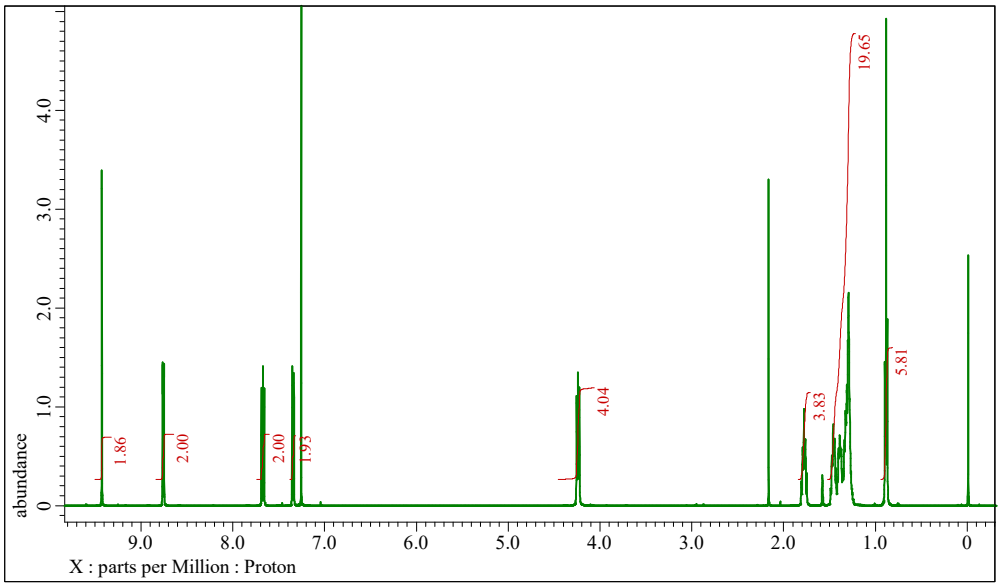

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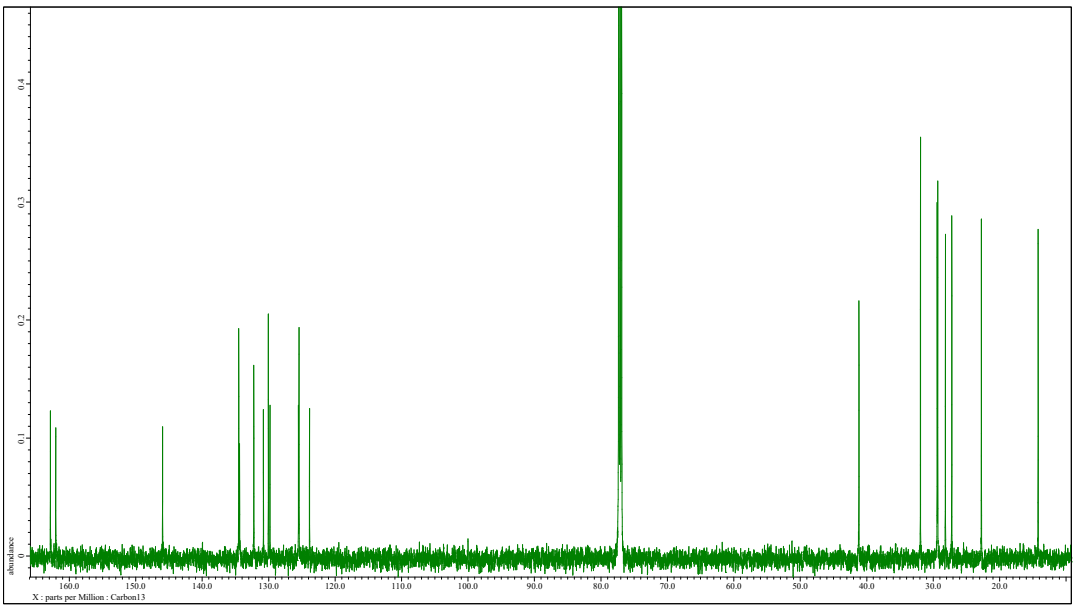

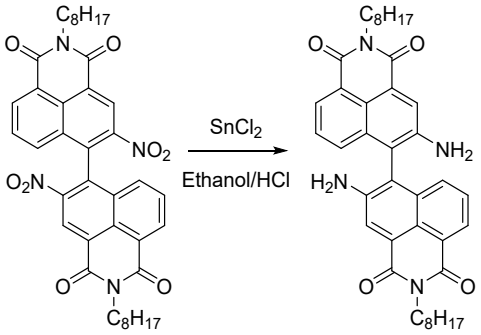

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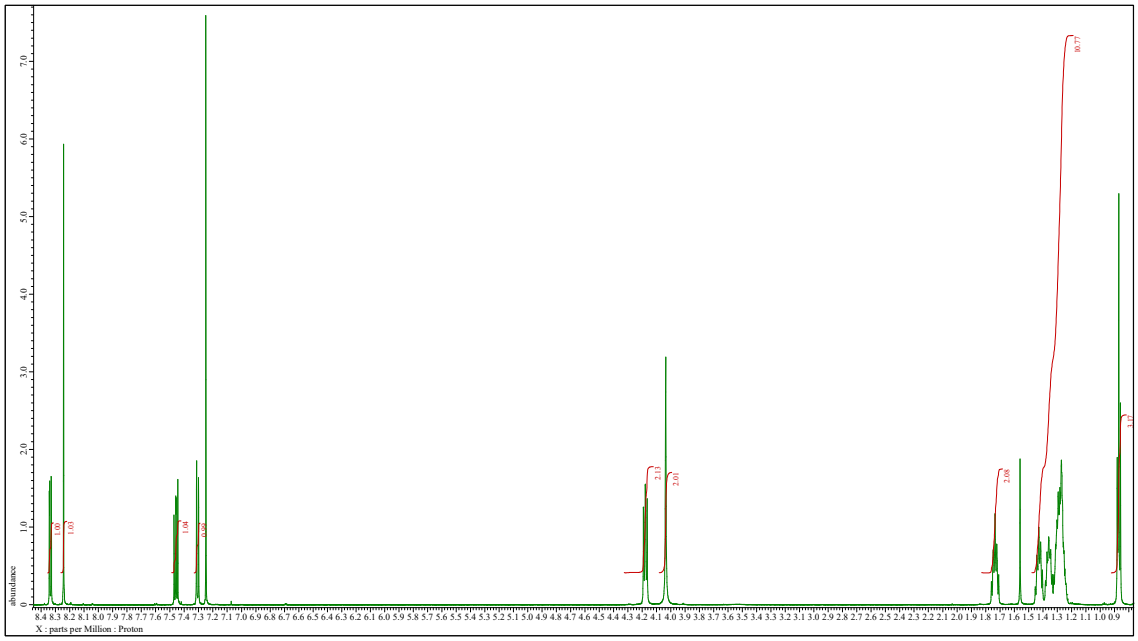

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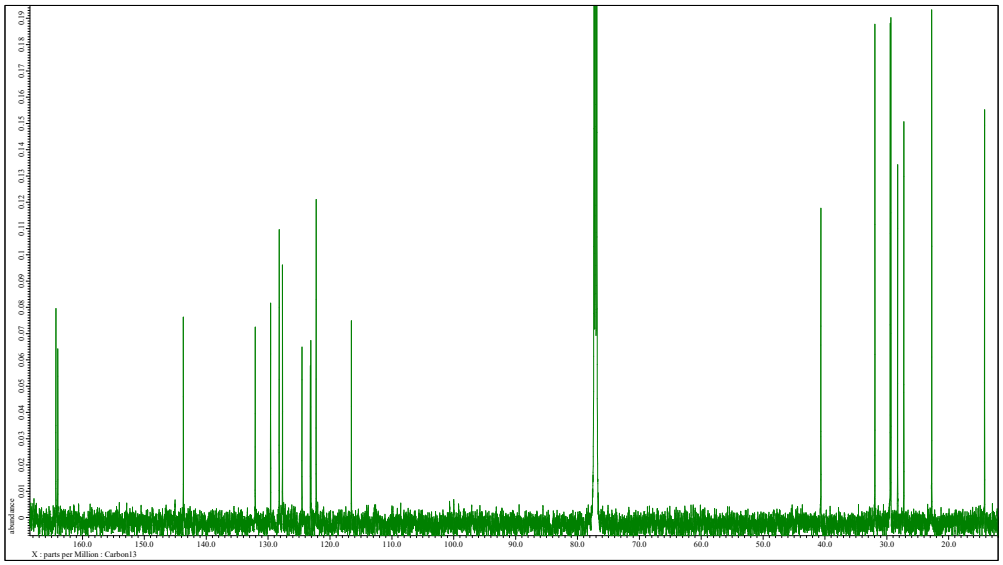

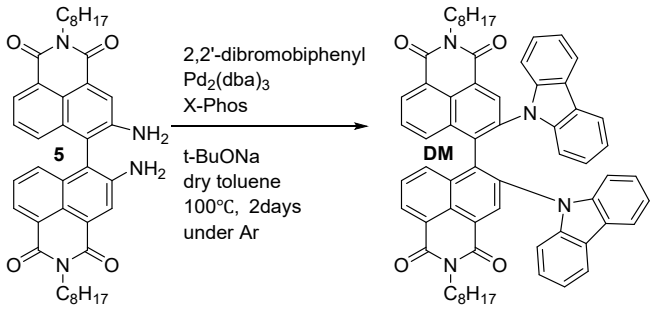

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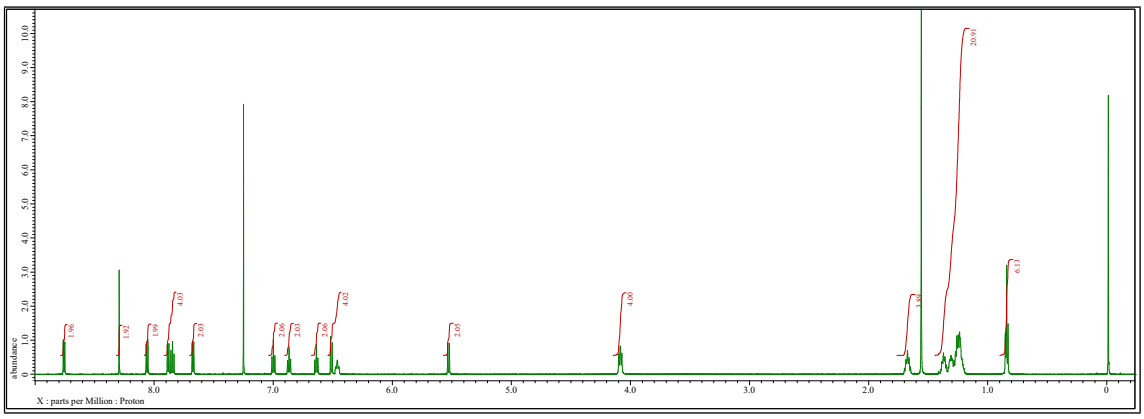

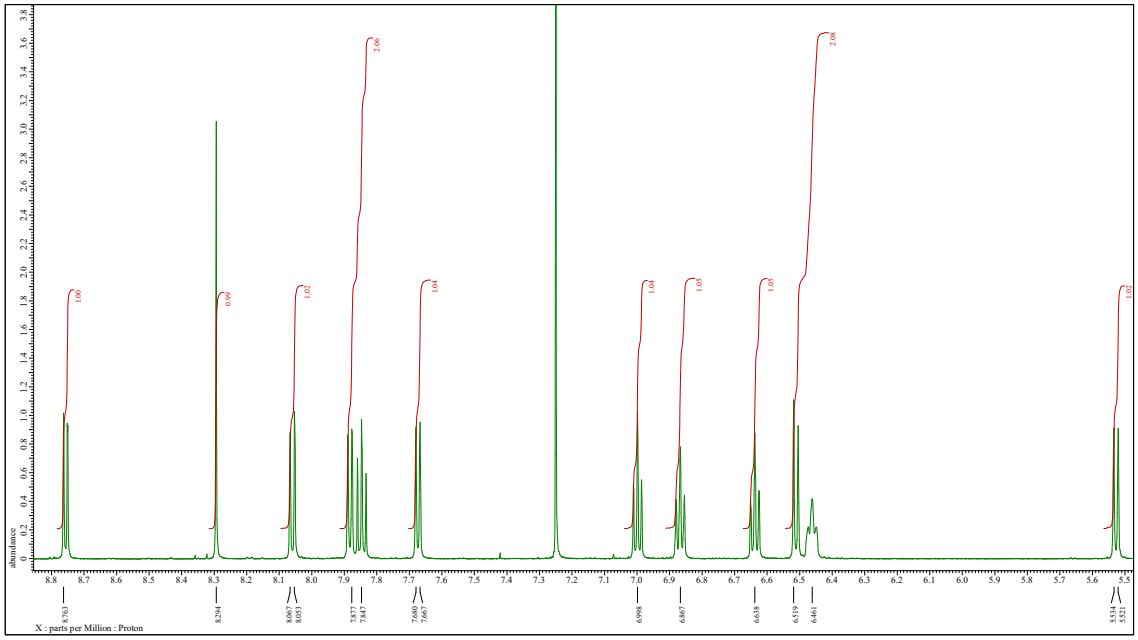

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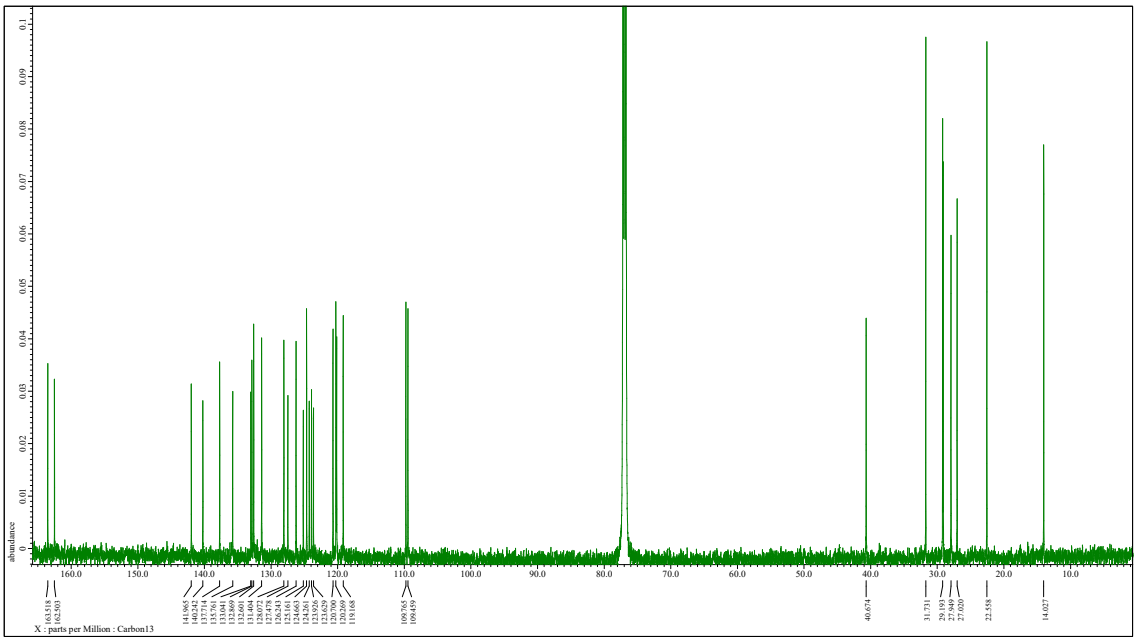
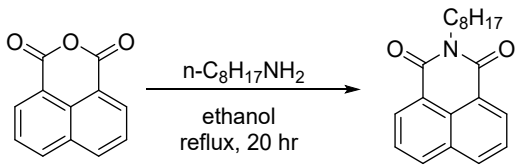
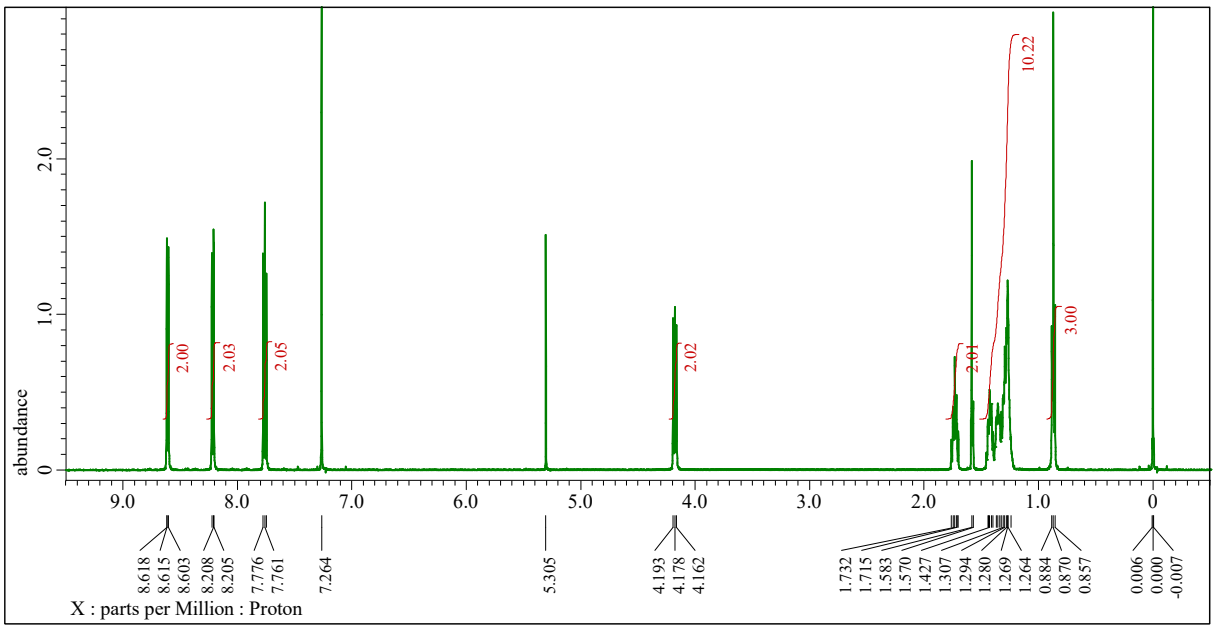




A

^{1}H NMR



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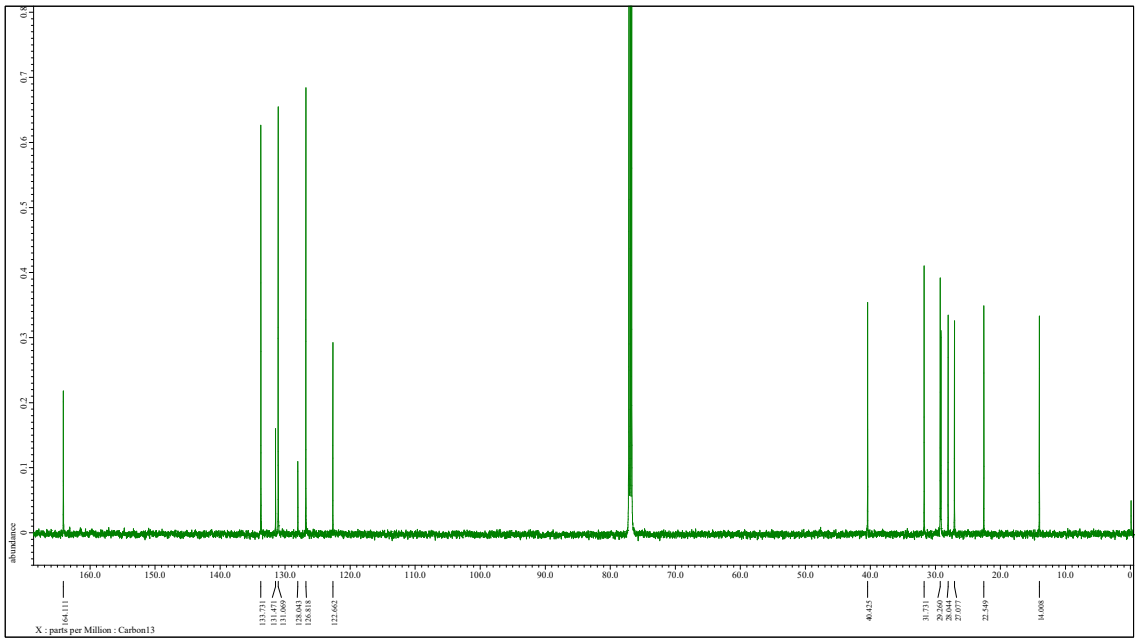

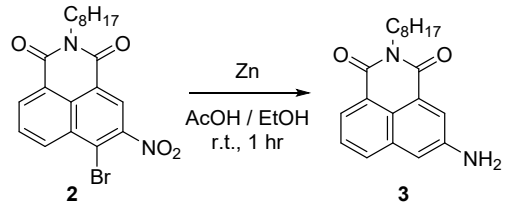

2 **3**

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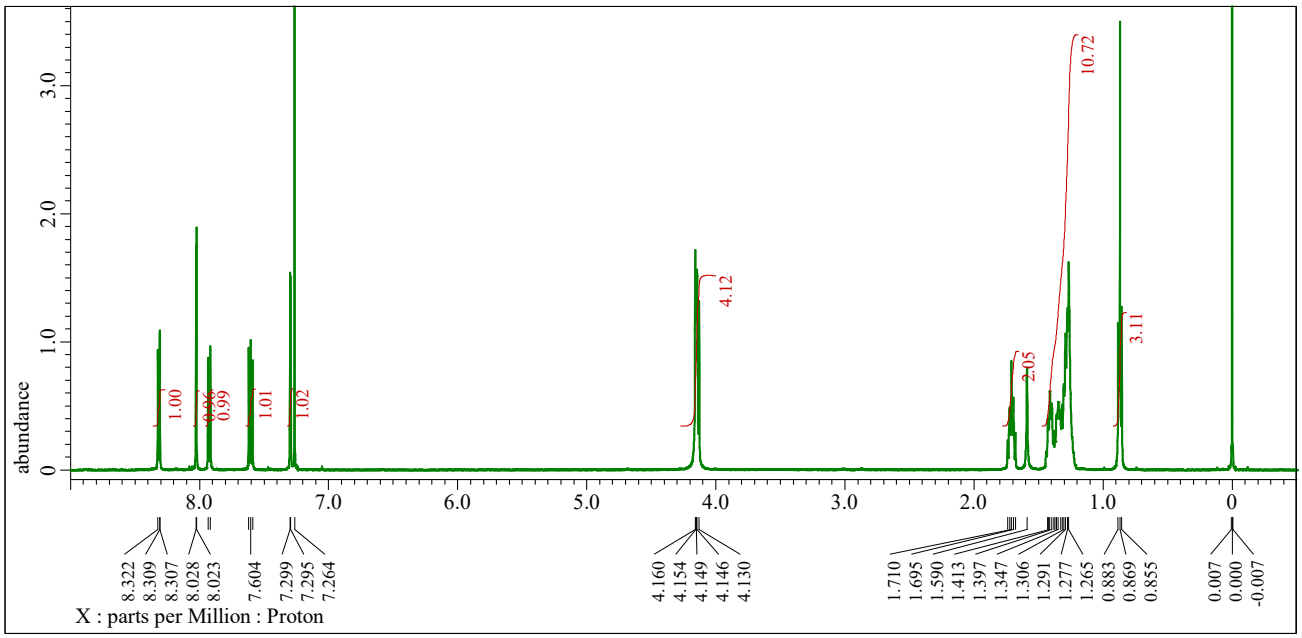

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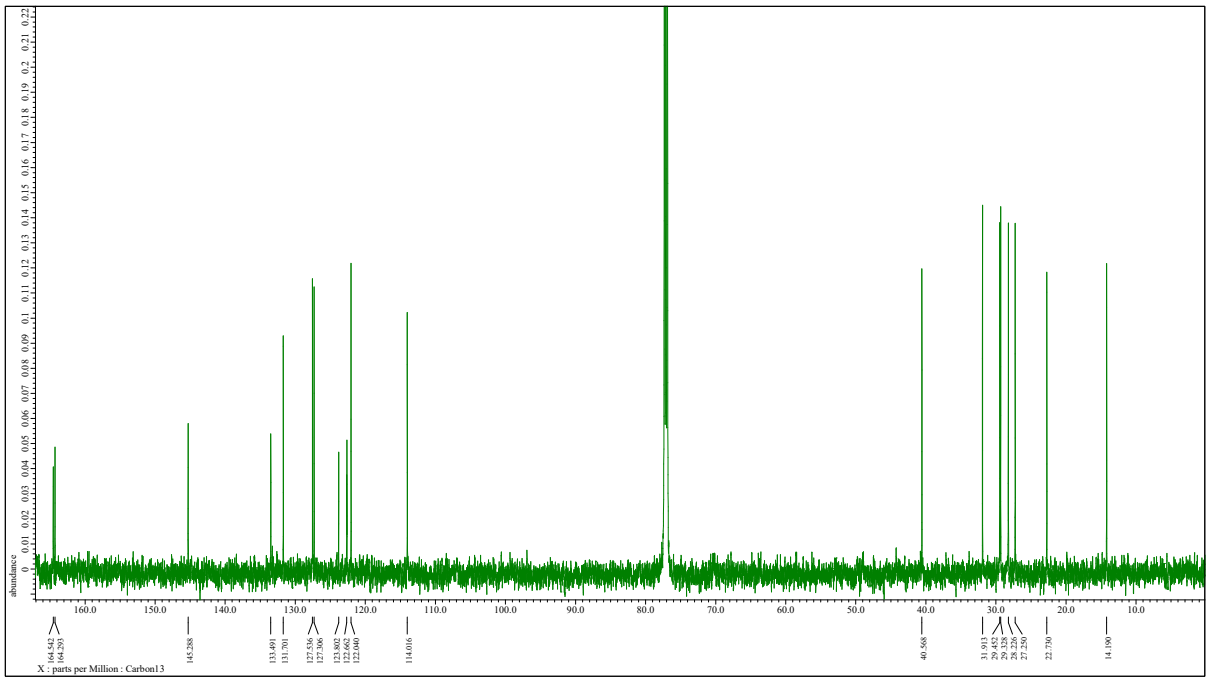

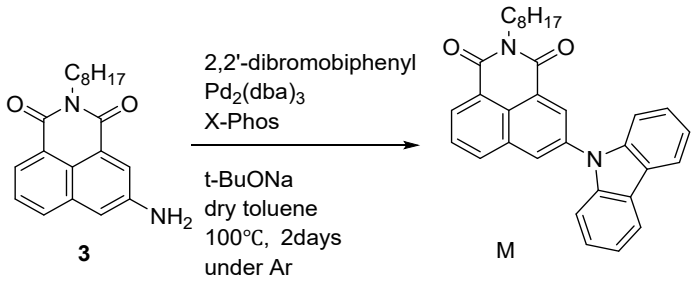

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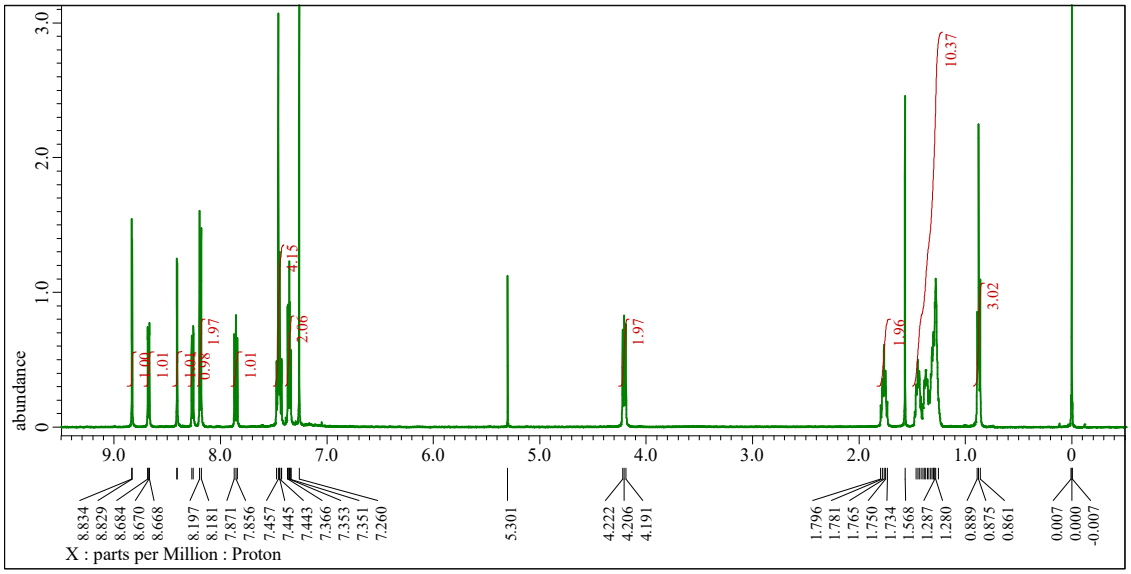

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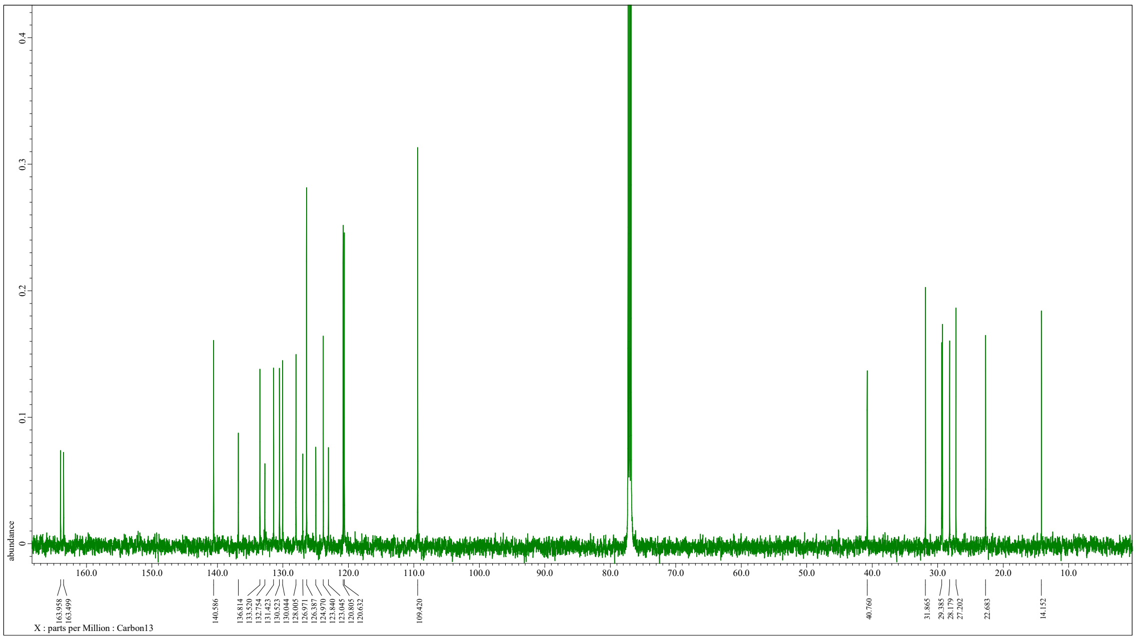

abundance
X : parts per Million : Carbon13
163.958
163.499
140.586
136.814
133.520
132.754
131.423
130.523
130.044
128.005
126.971
126.387
124.970
123.840
123.045
120.805
120.632
109.420
40.760
31.865
29.385
28.179
27.202
22.683
14.152

Nitration crude NMR

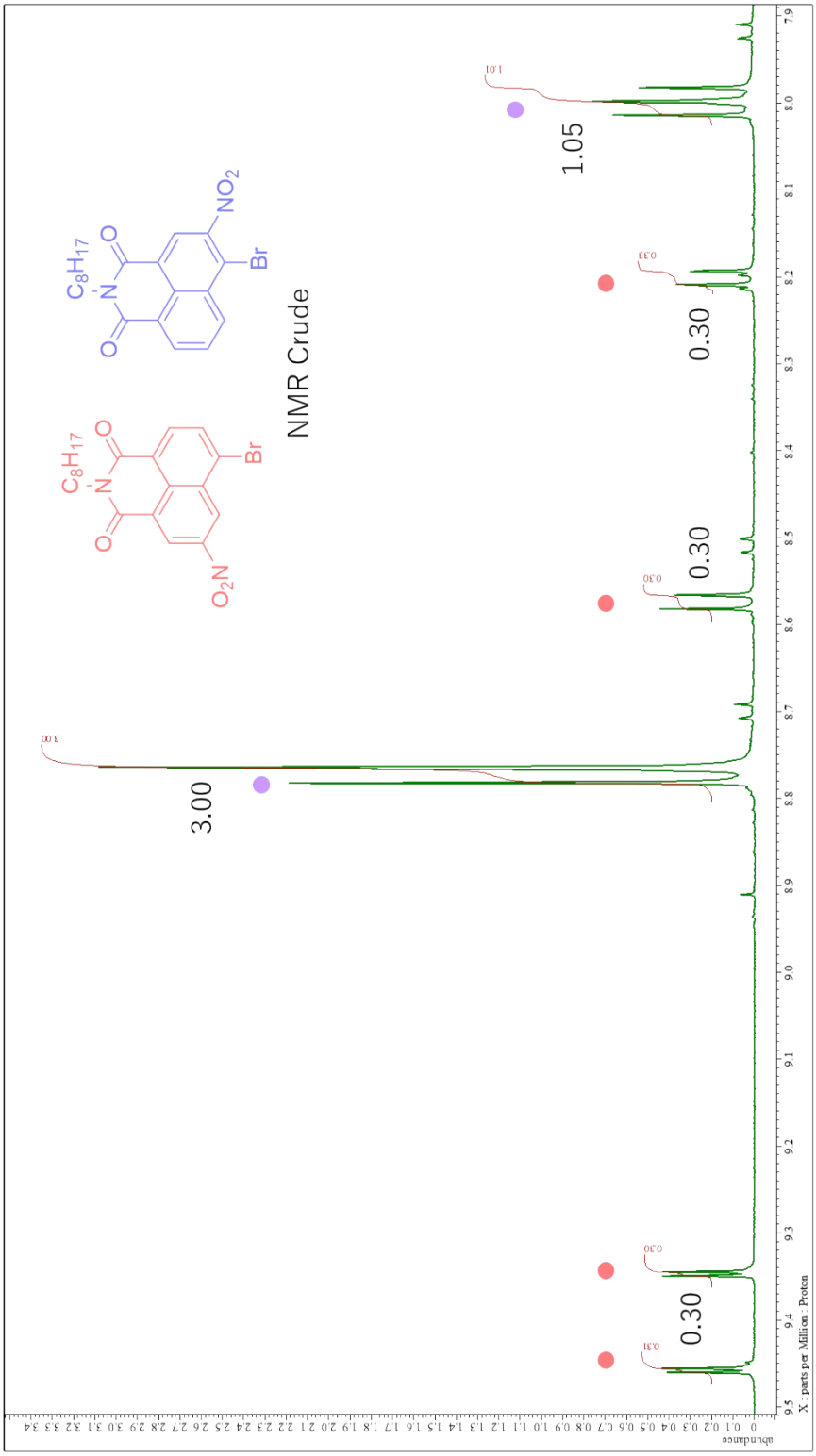


Figure S1: Crude NMR of the mixture obtained after nitration.

Thermogravimetry

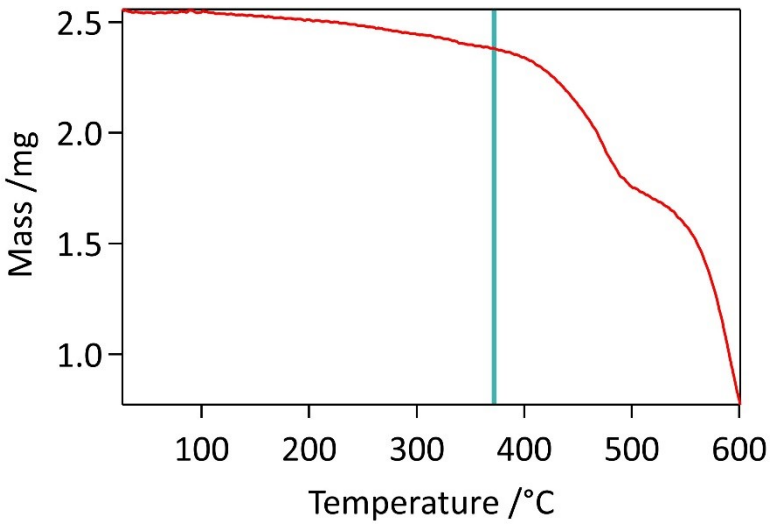


Figure S2: Thermogravimetric analysis of DM. The blue line indicates the point at which 5% of weight loss is observed, which happens at 372°C.

DFT and TD-DFT calculation results of M and DM

Table S1: The excitation energies of S_1, T_1 and T_2 state and ΔE_{ST} calculated at the TD-CAM-B3LYP/6-31G(d) level. Geometry optimization of the ground-state was performed at the CAM-B3LYP/6-31G(d).

Compound	S_1 (eV)	T_1 (eV)	T_2 (eV)	ΔE_{ST} (eV)
M	3.480	2.210	3.092	1.270
DM	3.199	2.048	2.239	1.151

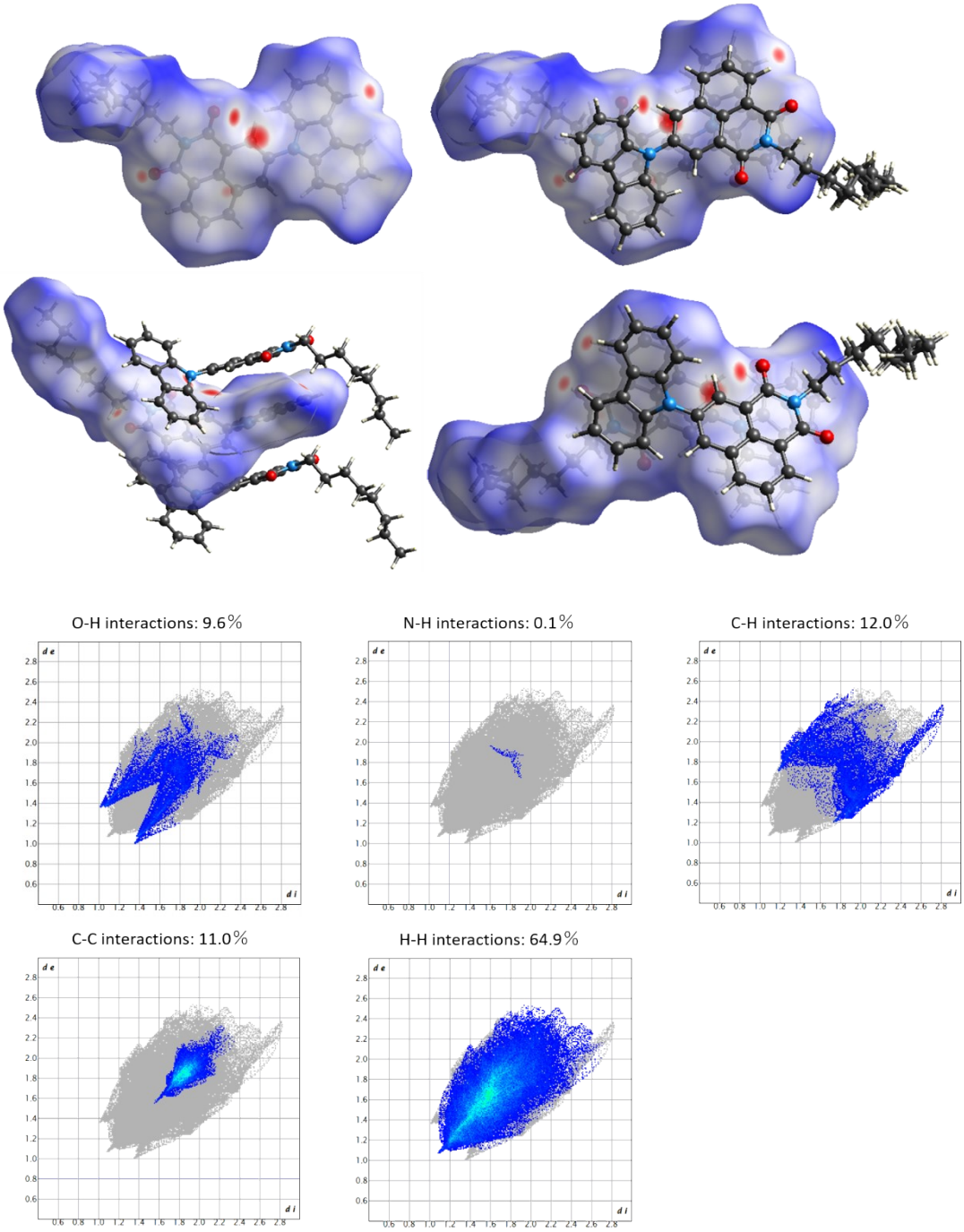


Figure S3: Hirshfield surface and Fingerprints plots of M generated by Crystal Explorer.

Chiral Separation

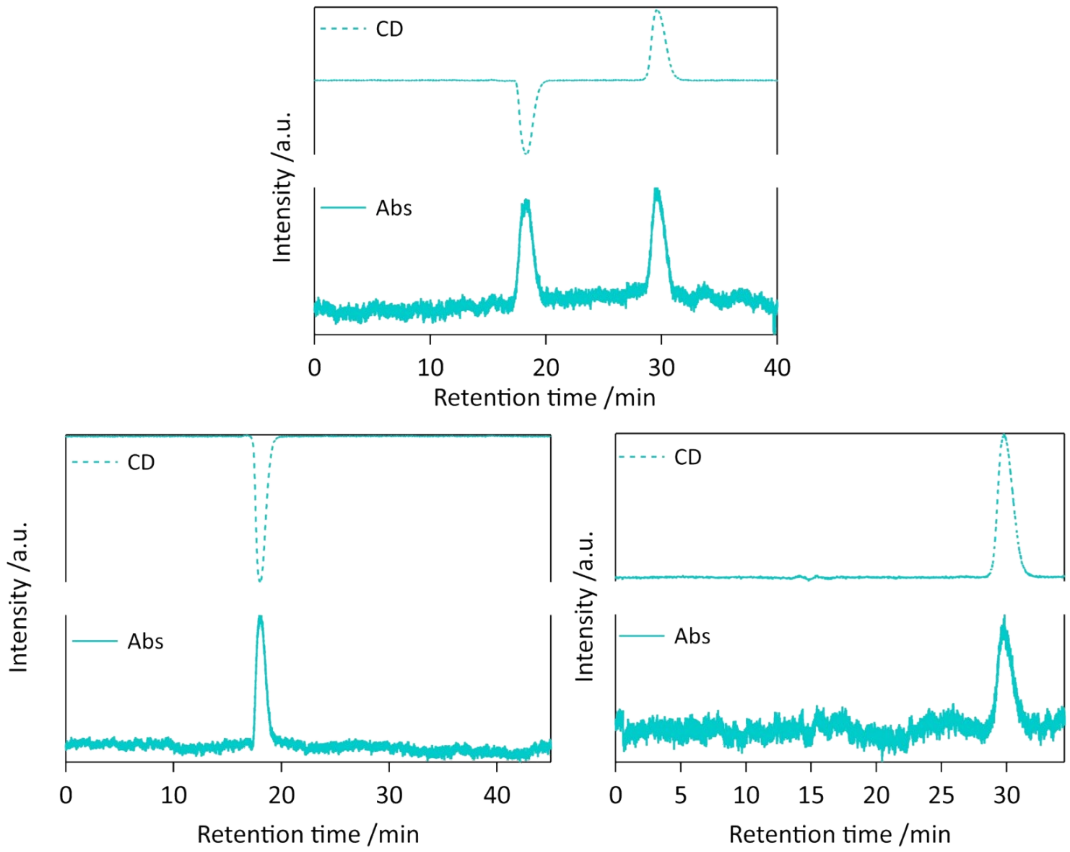


Figure S4: CD and UV signal from Chiral HPLC analysis. Top: Racemic mixture. Bottom: After separation, enantiomers S (left) and R (right) were successfully isolated.

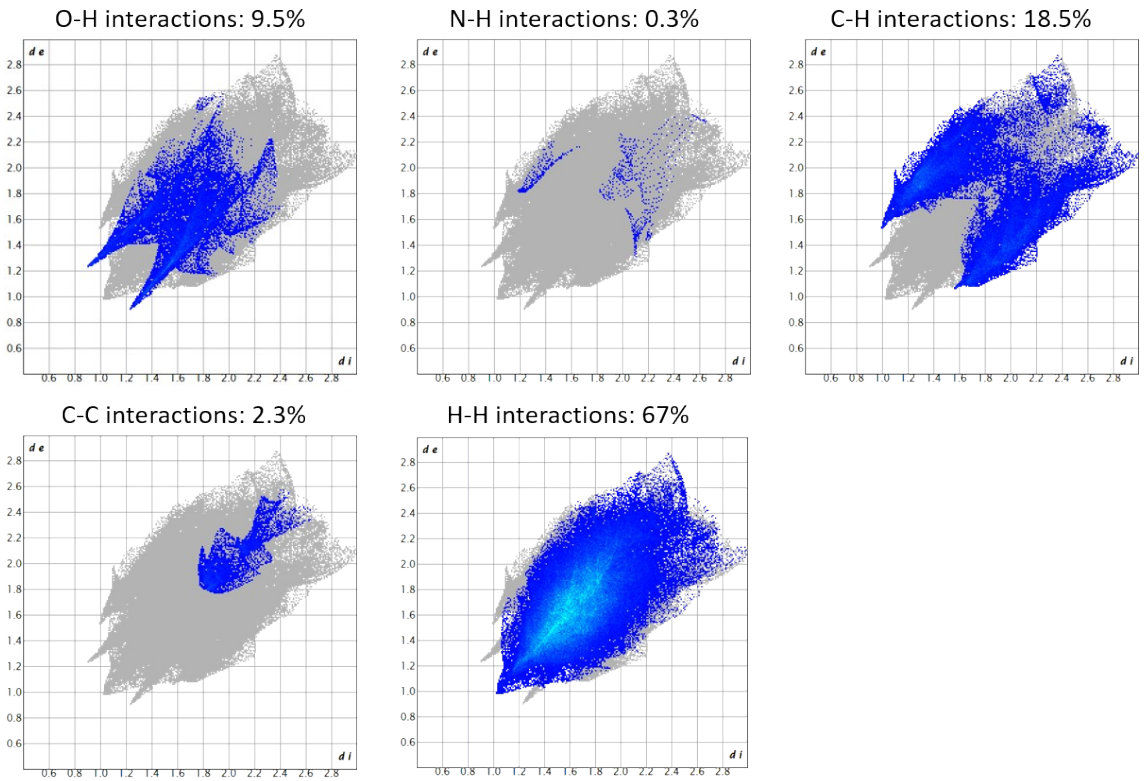


Figure S5: Fingerprint plots of DM calculated from Hirshfeld surface analysis highlighting different types of interactions.

Crystallography Analysis

Table S2: Crystallographic parameters and refinements details for achiral **M** and R enantiomer of **DM** (CCDC: 2237859 and 2237866)

Compound	Monomer **M**	Dimer **DM**
Recrystallization method	Slow evaporation of a mixture of 50/50 DCM/Methanol	Slow diffusion of hexane in a concentration solution of compound in chloroform
CCDC	2237859	2237866
Empirical formula	C32 H30 N2 O2	C64 H58 N4 O4
Crystal size, mm^3	X	0.2 x 0.09 x 0.02
Crystal system	Triclinic	monoclinic
Space group	$P\bar{1}(2)$	P21
a, Å	7.965(3)	13.8682(4)
b, Å	13.578(6)	30.7989(9)
c, Å	23.645(10)	19.9110(5)
α, °	83.988(6)	90.000
β, °	84.232(7)	109.9290(17)
γ, °	81.323(6)	90.000
Cell volume, Å3	2504.66(18)	7995.2(4)
Z ; Z'	4 ; 2	2 ; 1
T, K	103.15	103,15
ρ calcd ($g\ cm^{-3}$)	1.258	1.216
Radiation type ; wavelength Å	Mo ; 0.71075	Mo ; 0.71075
F_{000}	1008	3112
μ, mm^{-1}	0.078	0.076
θ range, °	2.187 - 25.350	2.187 - 25.351
Reflections unique	0.1311 (4640)	0.0728 (16222)
wR2 (all data)	0.3926 (9134)	0.1939 (29230)

Solvatochromism

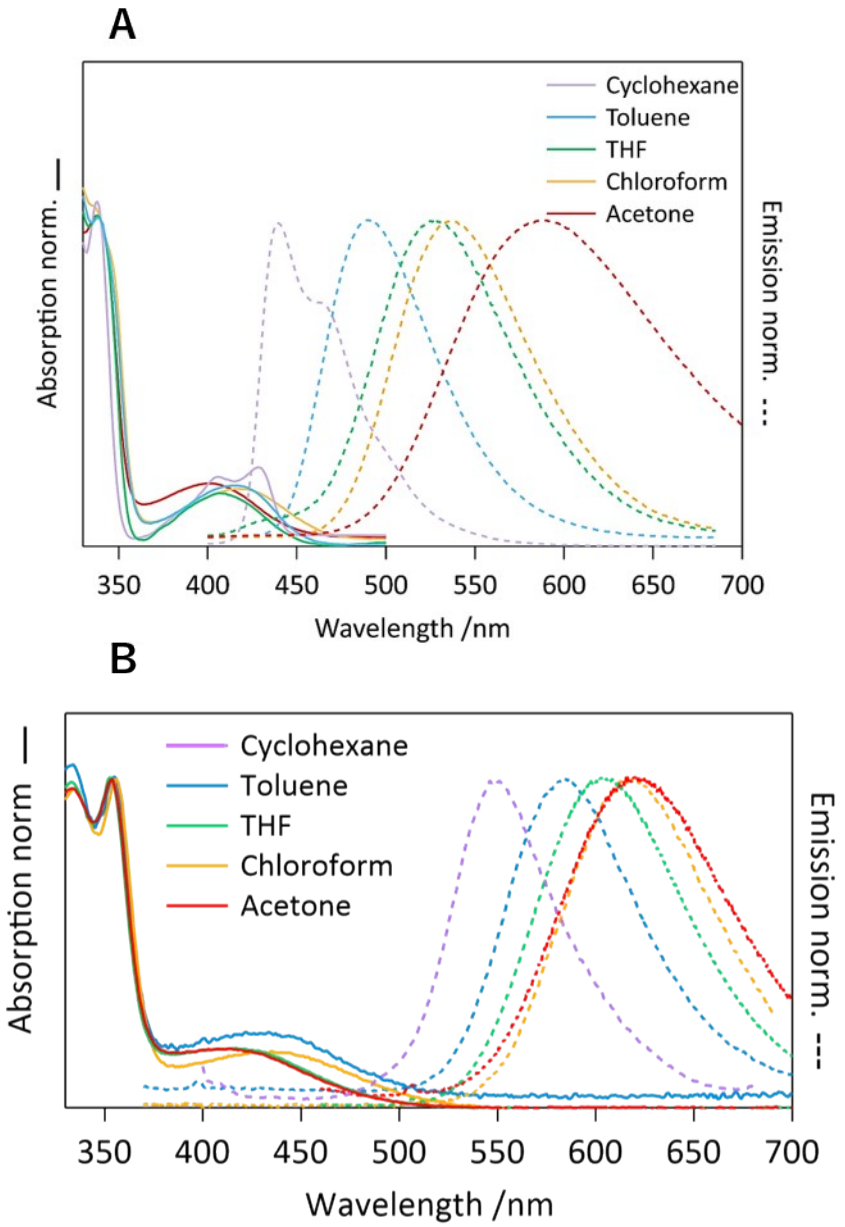


Figure S6: Solvatochromic measurements of (**A**) **M** and (**B**) **DM** in cyclohexane (violet), toluene (blue), tetrahydrofurane (THF), chloroform (orange) and acetone (red). Absorption in full line and Emission in dotted line. The absorption of **DM** in cyclohexane is not shown. The compound never really dissolved creating small aggregates and no clean absorption spectra has been obtained. λ_{exc} = 350 nm.

Photophysical Decays

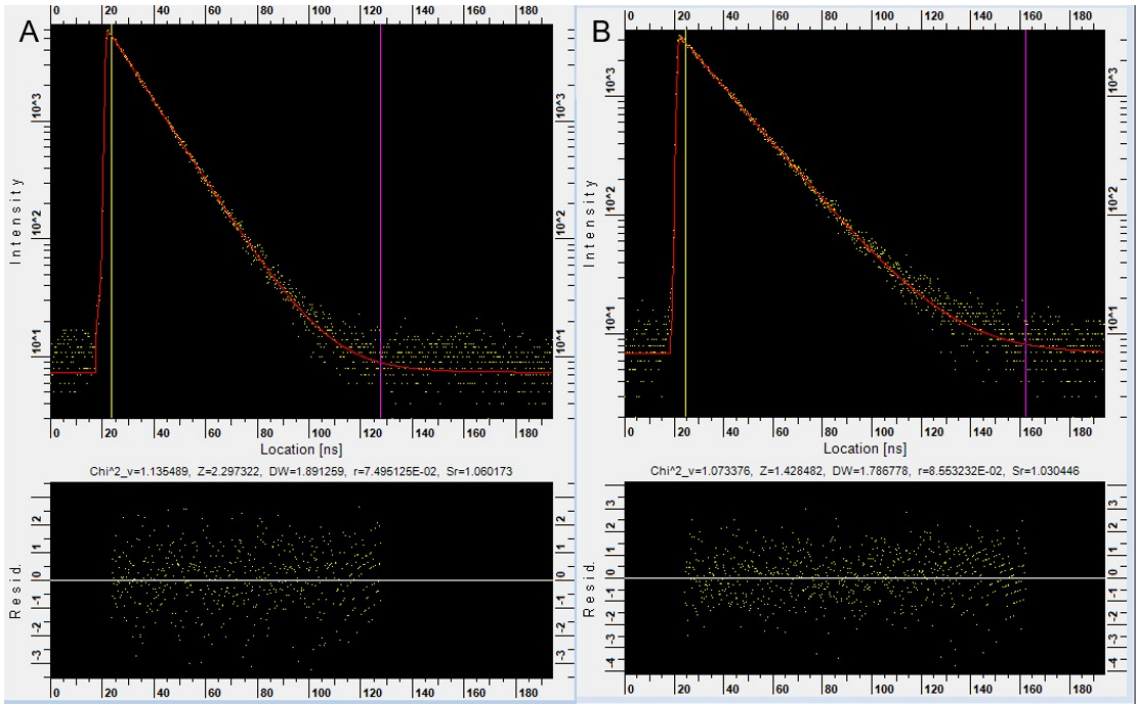


Figure S7: Fluorescence decays and residues of AlkylHalf measured in toluene in air (Left) and argon (Right) with χ^2 values of 1.14 and 1.07 respectively**.** λ_{exc} = 400 nm.

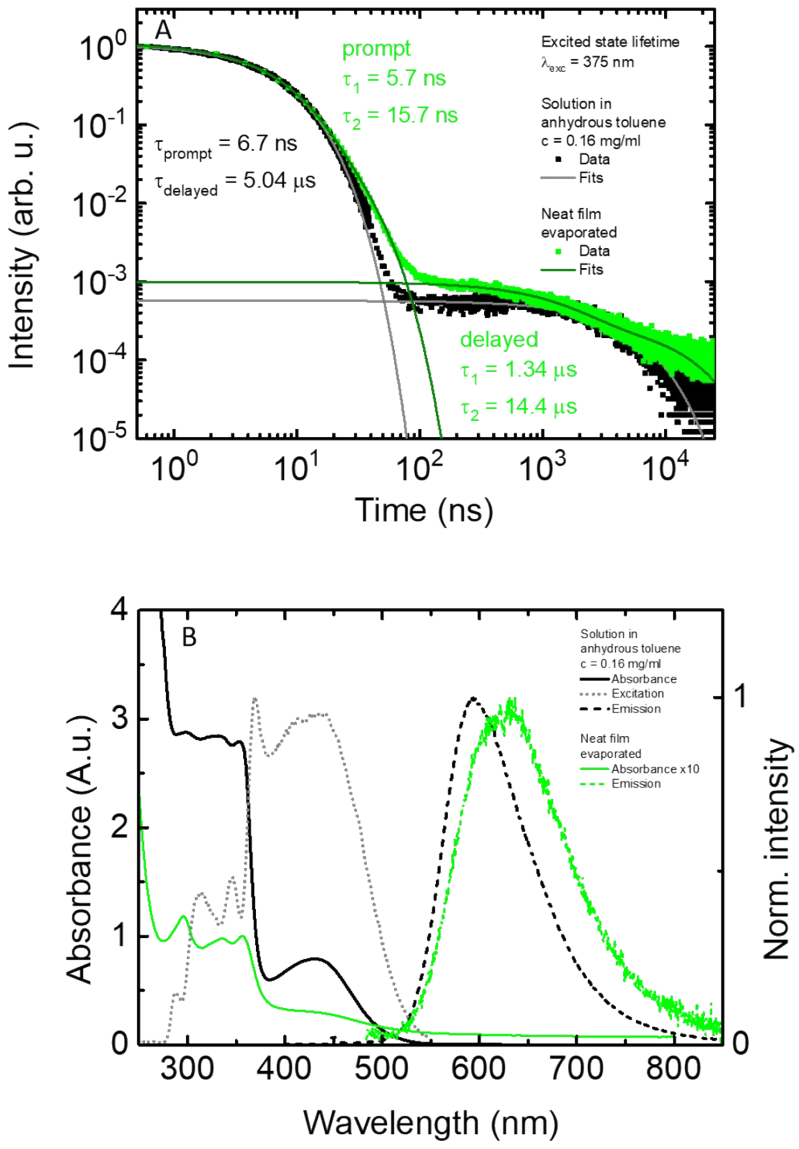


Figure S8: A. DM decays recorded in toluene solution (black) and in PMMA films (green) along with fitting curves and lifetimes values. **B**. DM absorption (full line), emission (dotted line) and excitation (dotted pale line) spectra in toluene (black) and in PMMA 10 wt% (green).

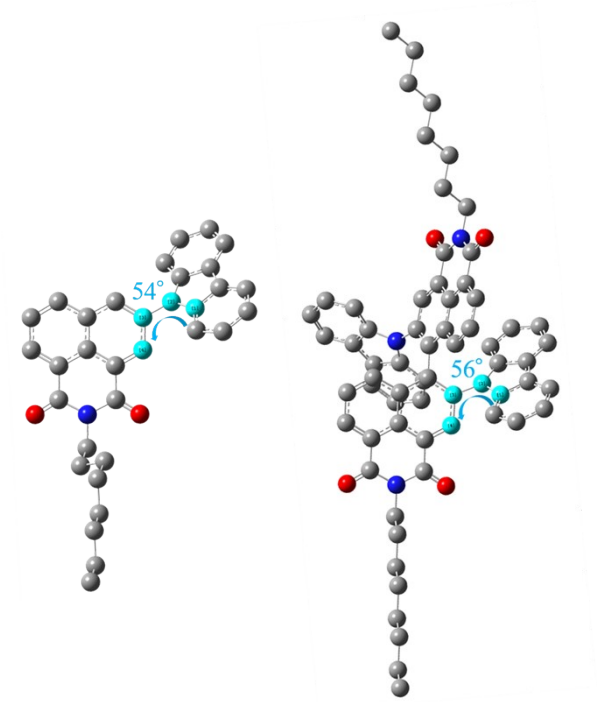


Figure S9: Relaxed ground state geometries of M and DM from DFT calculations with donor-acceptor dihedral angles (θ_{AD}) indicated in light blue.

Low temperature measurements

Toluene

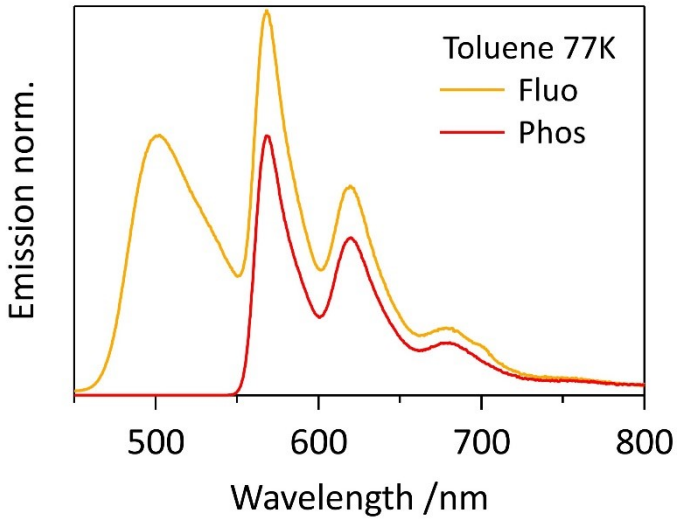


Figure S10: Emission spectra obtained for **DM** in cryostat at 77 K in toluene (C=50 µM). Direct emission in yellow and 75 ms delayed emission in red, revealing highly structured phosphorescence emission.

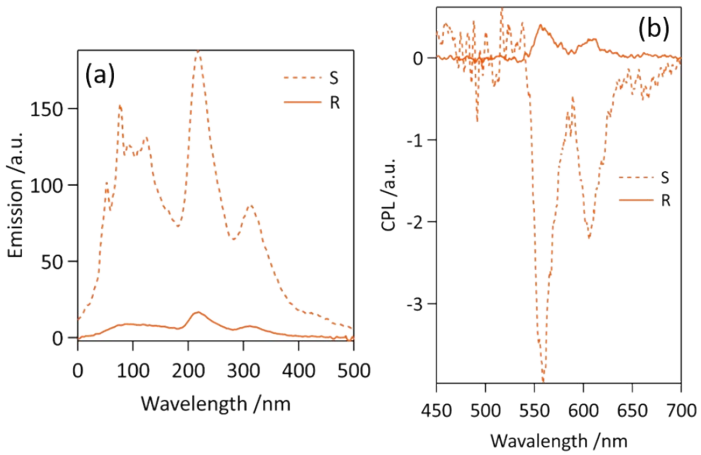
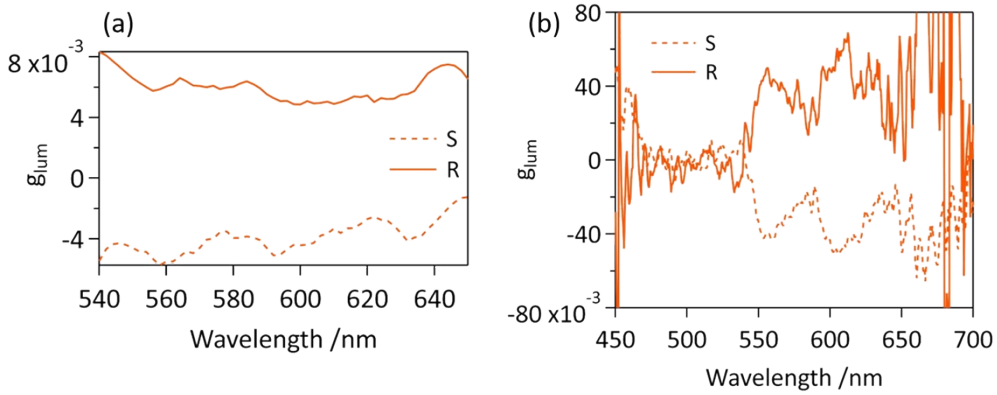


Figure S11: (a) Non-normalized emission spectra obtained for **DM** in cryostat at 77 K in MeTHF **(b)** Non-normalized CPL at 77 K under 375 nm excitation in MeTHF. (C= 50 mM, λ_{exc}=350 nm).



Figu

re S12: Representation of g_{lum} value as function of the wavelength for **DM (a)** at room temperature in toluene **(b)** at 77 K in MeTHF. (C= 50 mM, λ_{exc}=350 nm).

Table S3: Calculations of **DM** electric transition dipole moments for the $S_1 \rightarrow S_0$, $S_2 \rightarrow S_0$, $T_1 \rightarrow S_0$, $T_2 \rightarrow S_0$ respectively. [a] All values are in atomic units (a.u.)

Alkyl dimer	μ (M_s = 0)[a]	μ (M_s = 1)[a]	μ (M_s = −1)[a]
$S_1 \rightarrow S_0$	0.269		
$S_2 \rightarrow S_0$	0.766		
$T_1 \rightarrow S_0$	2.10×10^{-4}	2.81×10^{-4}	2.81×10^{-4}
$T_2 \rightarrow S_0$	3.46×10^{-4}	1.98×10^{-4}	1.98×10^{-4}

These values were obtained with the following method: TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) and PCM model (solvent = toluene).

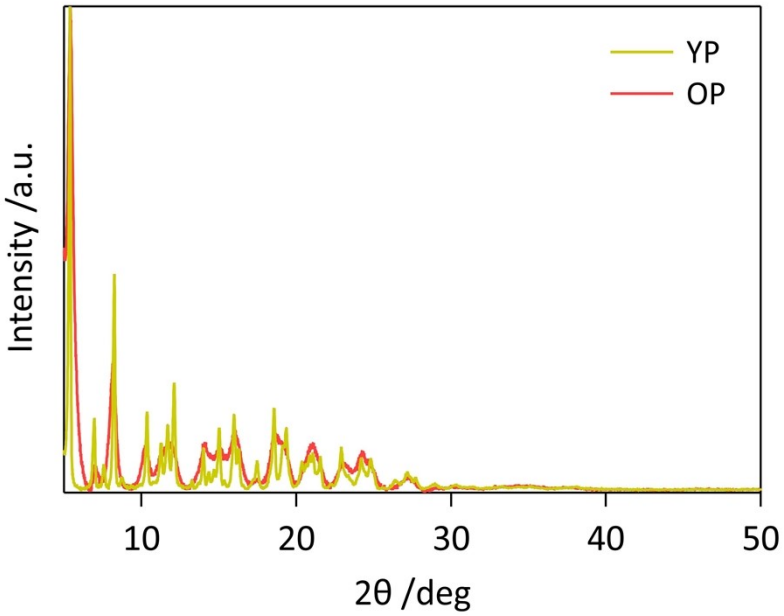


Figure S13: PXRD obtained from the yellow powder (**YP**) and orange powder (**OP**).

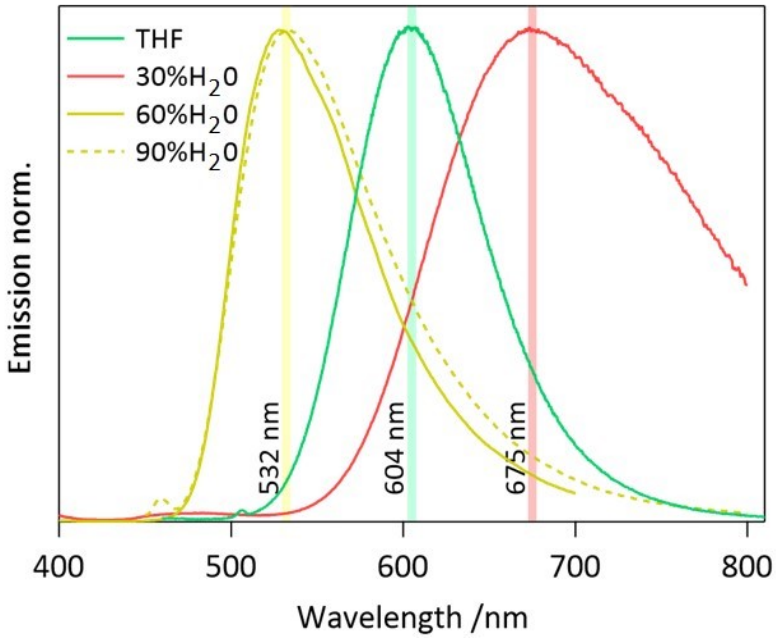


Figure S14: Emission of THF/H_2O solutions with their respective maximum. λ_{exc}=350 nm.

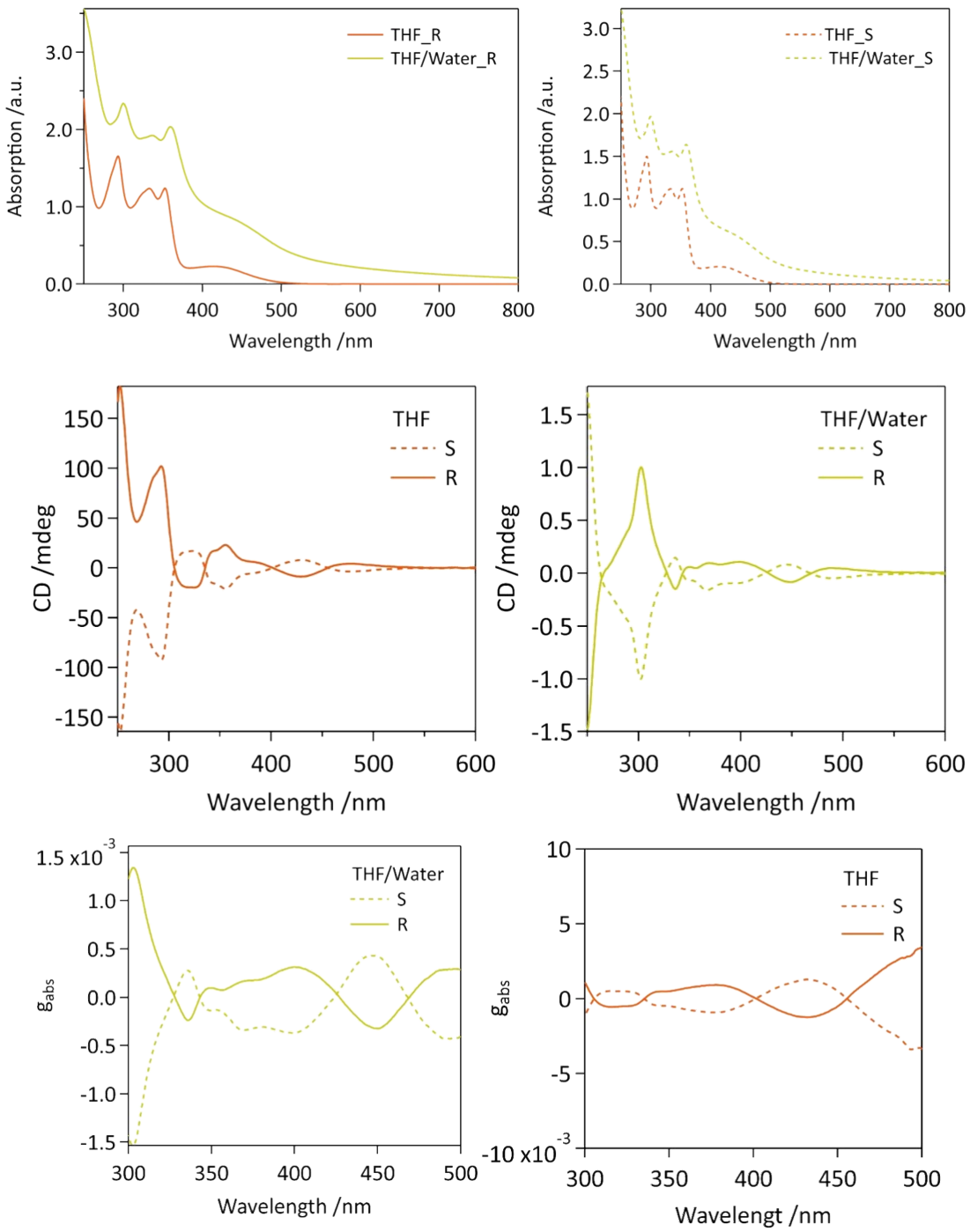


Figure S15: Top: Absorption spectra of *S* (dotted line) and *R* (full line) enantiomer in THF and THF/Water (10/90) respectively in orange and yellow. **Middle:** Enantiomers CD spectra. **Bottom:** *R* and *S* calculated gabs.

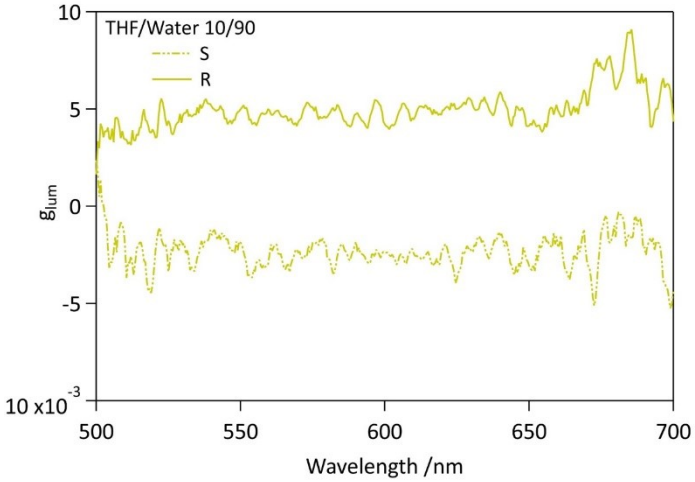


Figure S16: THF/water 90/10 g_{lum} value as function of the wavelength.

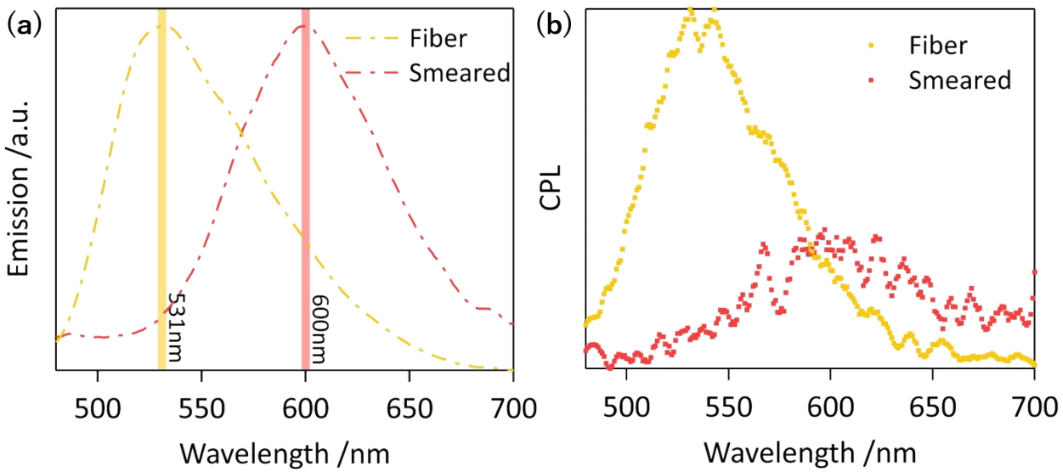


Fig. S17: **(a)** Emission spectra obtained for enantiopure *R* gel fibres before and after smearing with a spatula. **(b)** CPL spectra obtained from the *R* fibres before and after smearing.

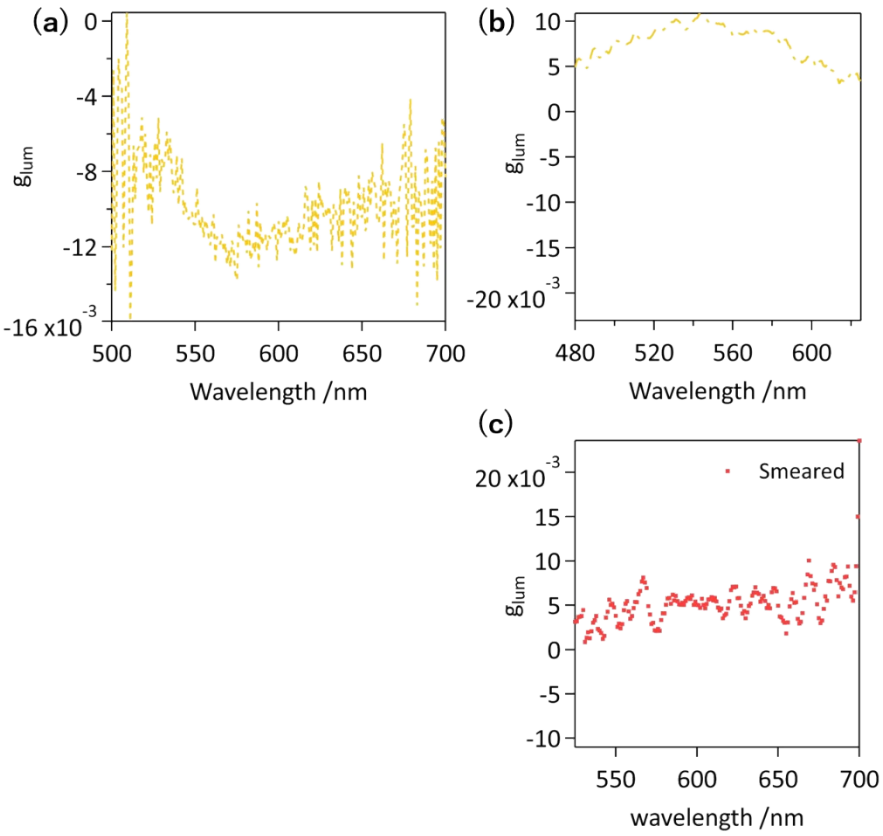


Fig. S18: g_{lum} values in function of wavelength **(a)** for enantiopure *S* fibres **(b)** for enantiopure *R* fibres **(c)** for *R* fibres after smearing.

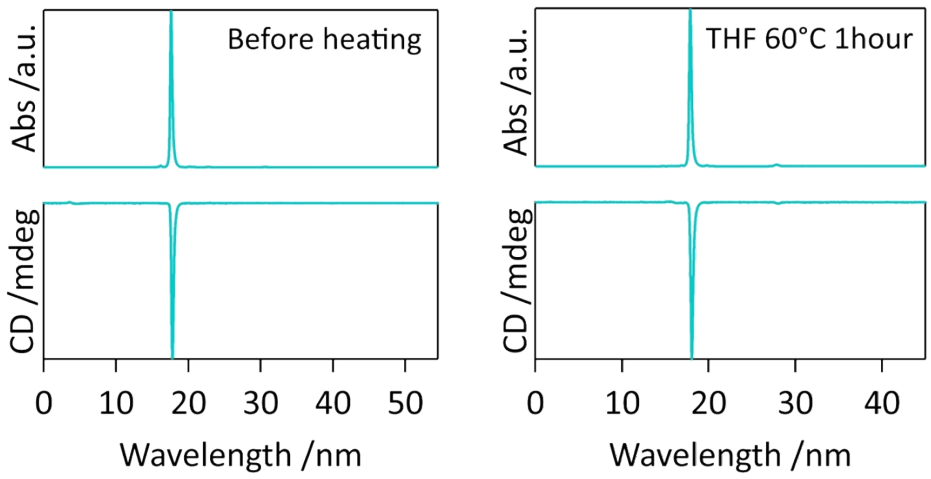


Figure S19: Racemization study of **DM** *S* enantiomer: the pure enantiomer was put through chiral

HPLC before and after heating at 60 degrees for 1 hour in THF.