Supporting Information

for

3,5-Dianilino Substituted Difluoroboron Dipyrromethene: Synthesis, Spectroscopy, Photophysics, Crystal Structure, Electrochemistry, and Quantum-Chemical Calculations

Wenwu Qin[#,†], Volker Leen[†], Wim Dehaen[†], Jie Cui [#], Chan Xu [#], Xiaoliang Tang[#], Weisheng Liu [#], Taoufik Rohand[†], David Beljonne[‡], Bernard Van Averbeke[‡], John N. Clifford[†], Kris Driesen[†], Koen Binnemans[†], Mark Van der Auweraer[†], and Noël Boens[*,†]

[#] *College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China*

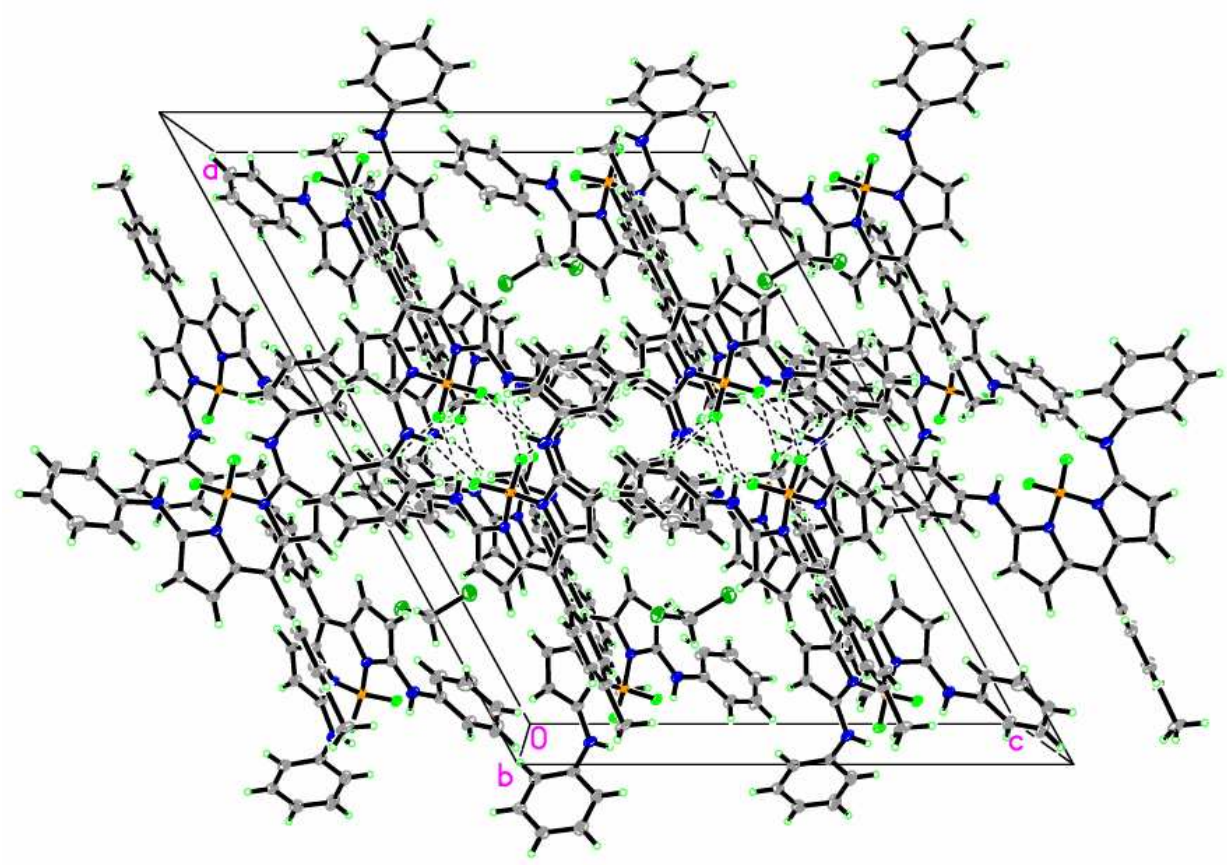
[†] *Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200f – bus 02404, 3001 Leuven, Belgium*

[‡] *Laboratory for Chemistry of Novel Materials, University of Mons-Hainaut, Place du Parc 20, 7000 Mons, Belgium*

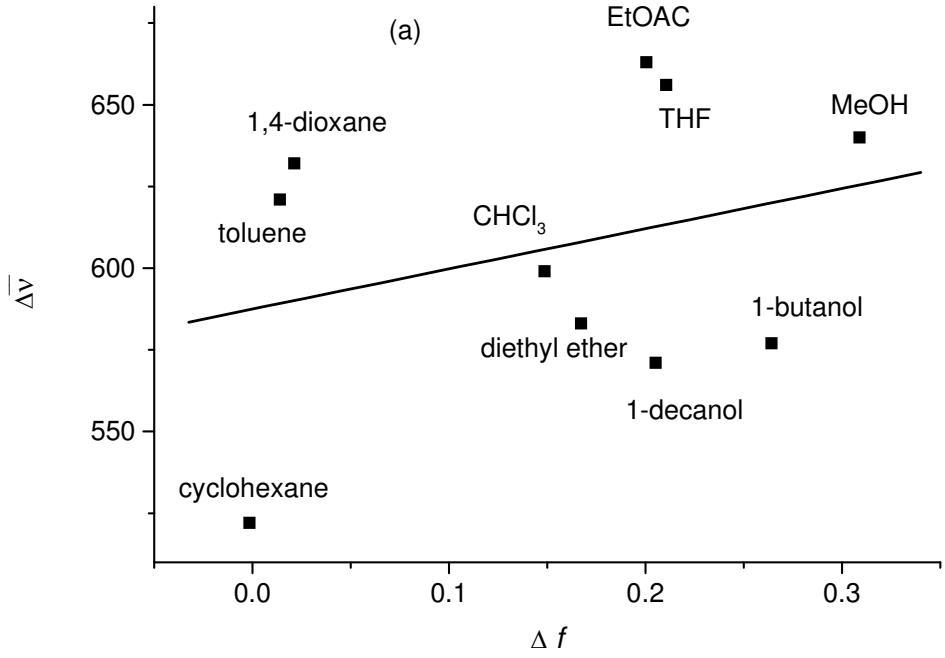
Table S1. Hydrogen bonds in the dimeric structure of **1**. Distances are in Å, angles are in degrees (°).

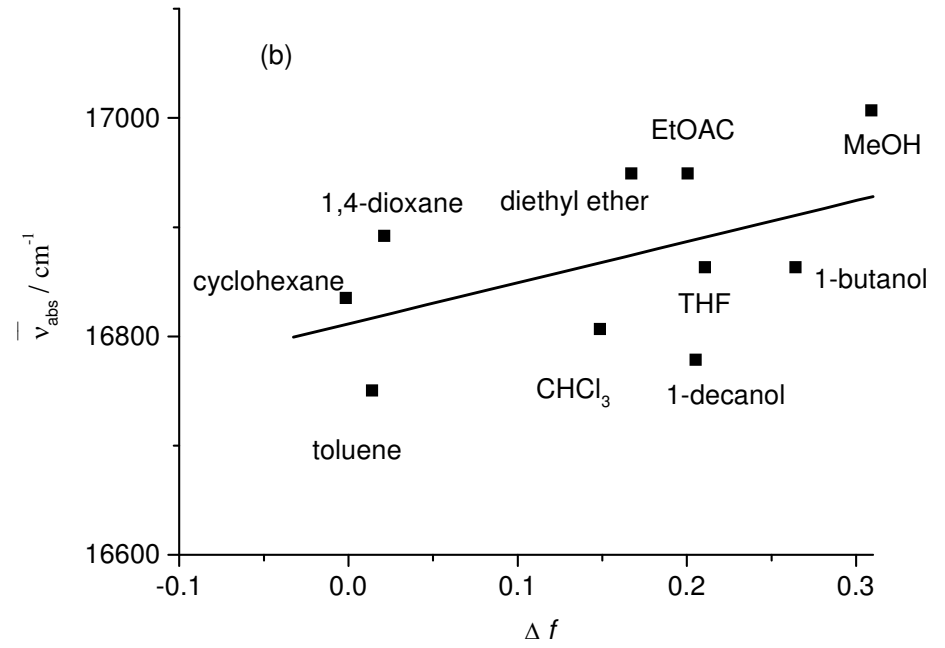
D—H···A	*d*(D—H)	*d*(H···A)	*d*(D···A)	∠D—H···A
N1—H1A···F1	0.8600	2.5200	3.012(5)	117.00
N1—H1A···F2	0.8600	2.5200	3.082(4)	124.00
N1—H1A···F2^{i}	0.8600	2.2800	3.091(5)	156.00
N2—H2A···F1	0.8600	2.4600	3.035(4)	125.00
N2—H2A···F2	0.8600	2.5200	3.041(5)	120.00
N2—H2A···F1^{i}	0.8600	2.4200	3.210(5)	153.00
C28—H28···F1^{i}	0.9300	2.4800	3.267(6)	142.00

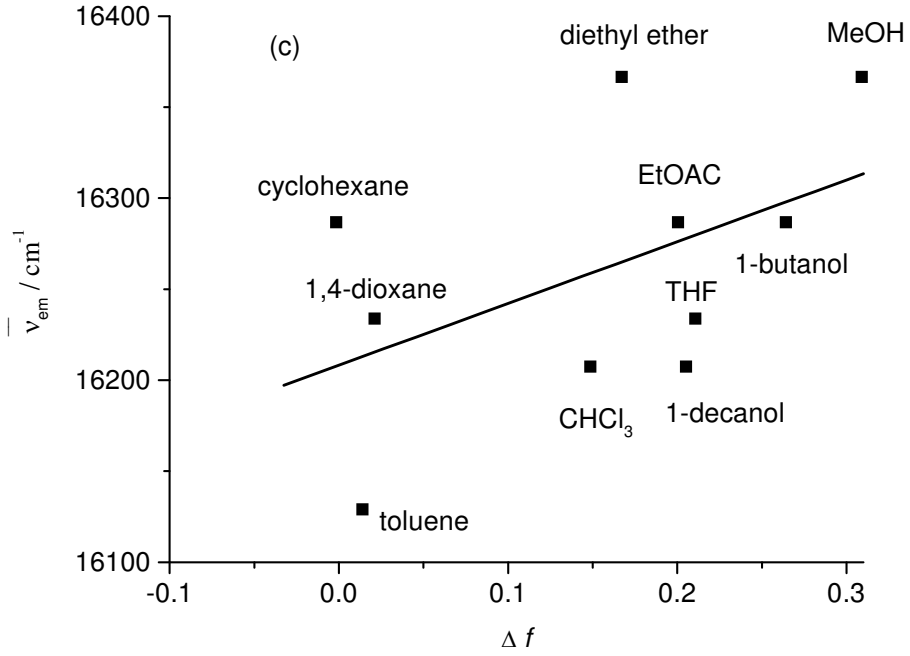
symmetry codes: *i*) -x, y, 1/2-z



↑ **Figure S1.** Aggregation of compound **1** through a series of hydrogen bonds and π–π stacking interactions in the crystal cell.


(a)
EtOAC
THF
MeOH
1,4-dioxane
toluene
CHCl3
1-butanol
diethyl ether
1-decanol
cyclohexane
650
600
550
0.0
0.1
0.2
0.3
Δ f
Δν


(b)
EtOAC
MeOH
1,4-dioxane
diethyl ether
cyclohexane
THF
1-butanol
CHCl3
1-decanol
toluene
17000
16800
16600
-0.1
0.0
0.1
0.2
0.3
Δ f
ν abs / cm-1



↑ **Figure S2.** Plots of (a) the Stokes shifts $\Delta\bar{\nu}$, (b) the absorption maxima $\bar{\nu}_{abs}$, and (c) the emission maxima $\bar{\nu}_{em}$ of **1** versus the Lippert solvent parameter Δf. The straight lines are the best linear fits (r = 0.302 for $\Delta\bar{\nu}$, r = 0.500 for $\bar{\nu}_{abs}$, r = 0.499 for $\bar{\nu}_{em}$) to the experimental values.

Comparison of the simple linear regressions for **1** of $\bar{\nu}_{abs}$ versus SP (eq 1a) and of $\bar{\nu}_{abs}$ versus SdP (eq 1b) shows that solvent polarizability (r = 0.850, Figure S3a) is a more important factor than solvent (di)polarity (r = 0.509, Figure S4a) inducing the solvent-sensitive shifts of the absorption band.

$$\bar{\nu}_{abs} = \bar{\nu}^{0}_{abs} + c_{SP}\,SP \qquad (1a)$$

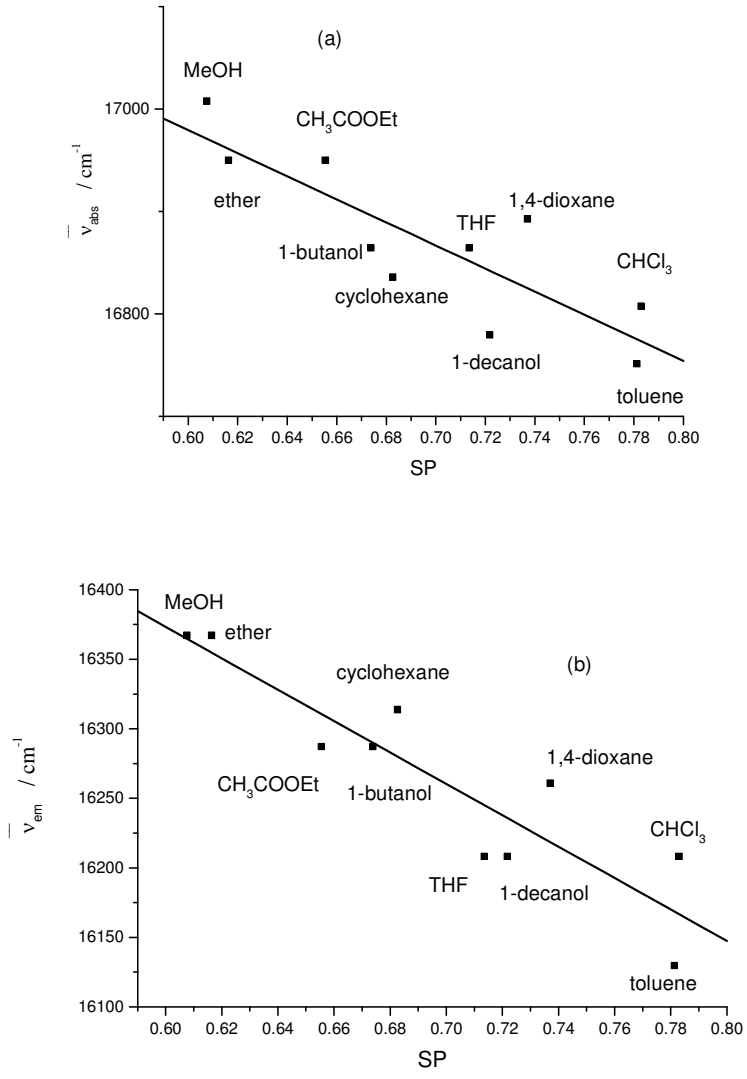
$$\bar{\nu}_{abs} = \bar{\nu}^{0}_{abs} + d_{SdP}\,SdP \qquad (1b)$$

Evaluation of the simple linear regressions for **1** of $\bar{\nu}_{em}$ versus SP (eq 2a) and of $\bar{\nu}_{em}$ versus SdP (eq 2b) shows that the solvent-dependent shifts of the emission are

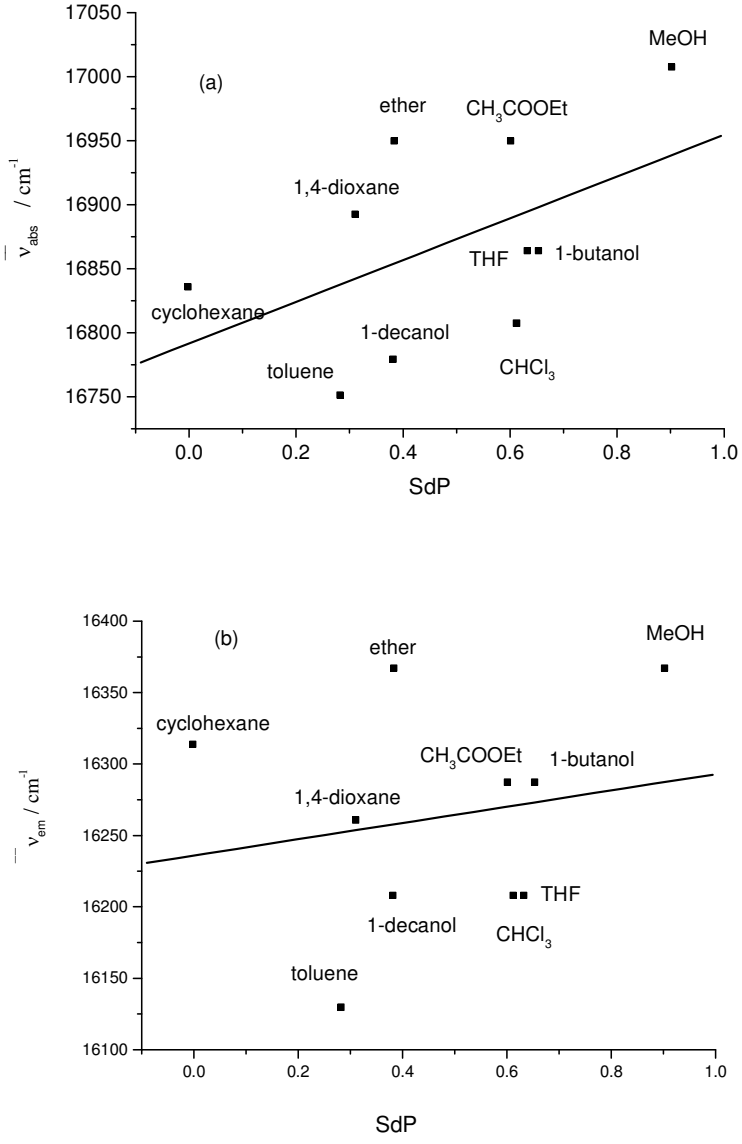
influenced much more by solvent polarizability (r = 0.910, Figure S3b) than by solvent (di)polarity (r = 0.190, Figure S4b).

$$\overline{\nu}_{em} = \overline{\nu}^{0}_{em} + c_{SP}\,SP \qquad (2a)$$

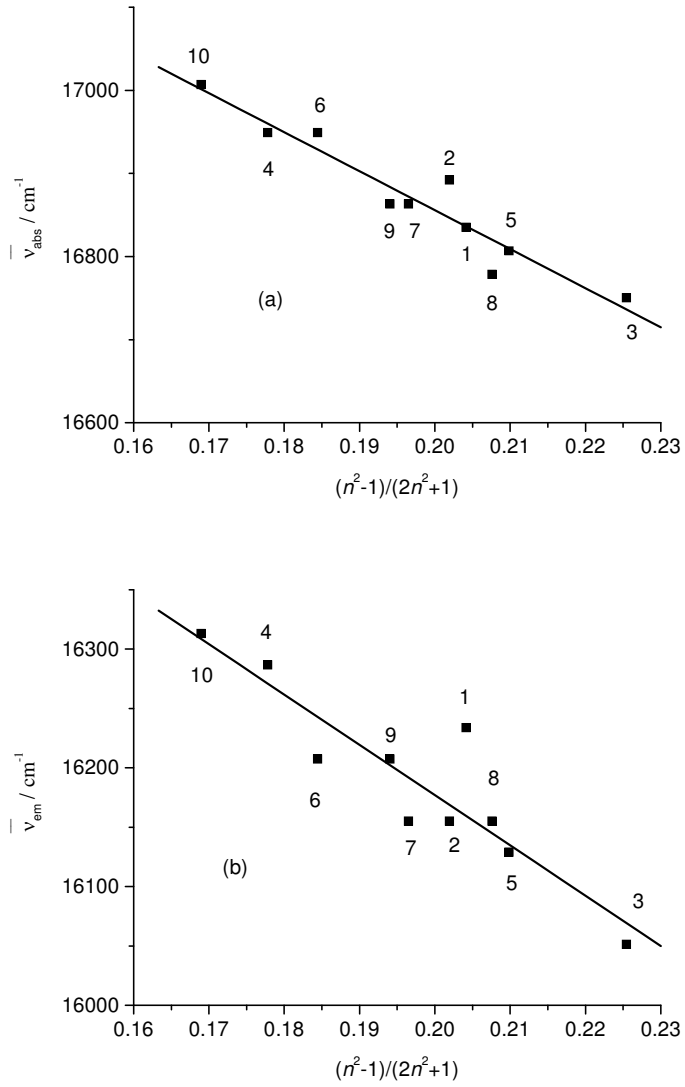
$$\overline{\nu}_{em} = \overline{\nu}^{0}_{em} + d_{SdP}\,SdP \qquad (2b)$$



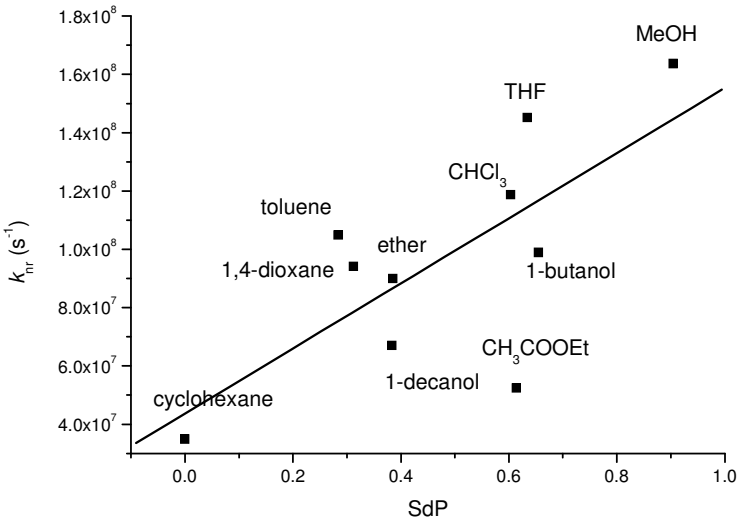
↑ **Figure S3.** Linear relationship between (a) the absorption maxima $\overline{\nu}_{abs}$ of **1** and SP (r = 0.850) and (b) the fluorescence emission maxima $\overline{\nu}_{em}$ of **1** and SP (r = 0.910).



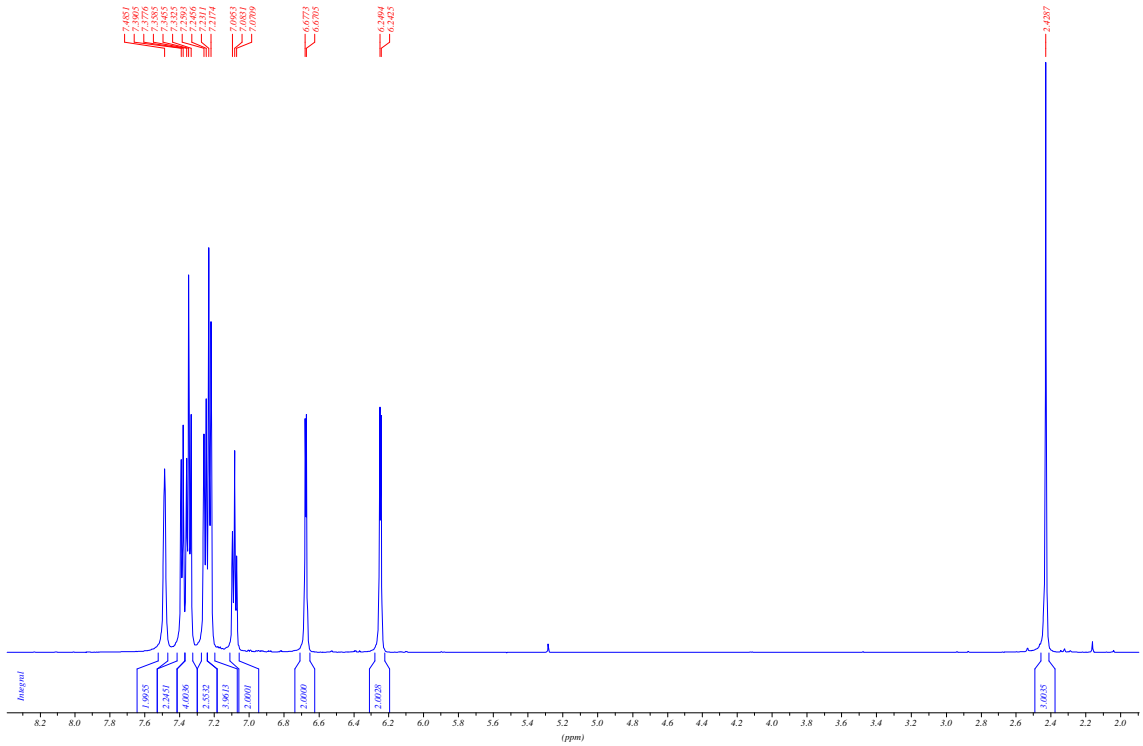
↑ **Figure S4.** Linear relationship between (a) the absorption maxima $\bar{\nu}_{abs}$ of **1** and SdP (r = 0.509) and (b) the fluorescence emission maxima $\bar{\nu}_{em}$ of **1** and SdP (r = 0.190).



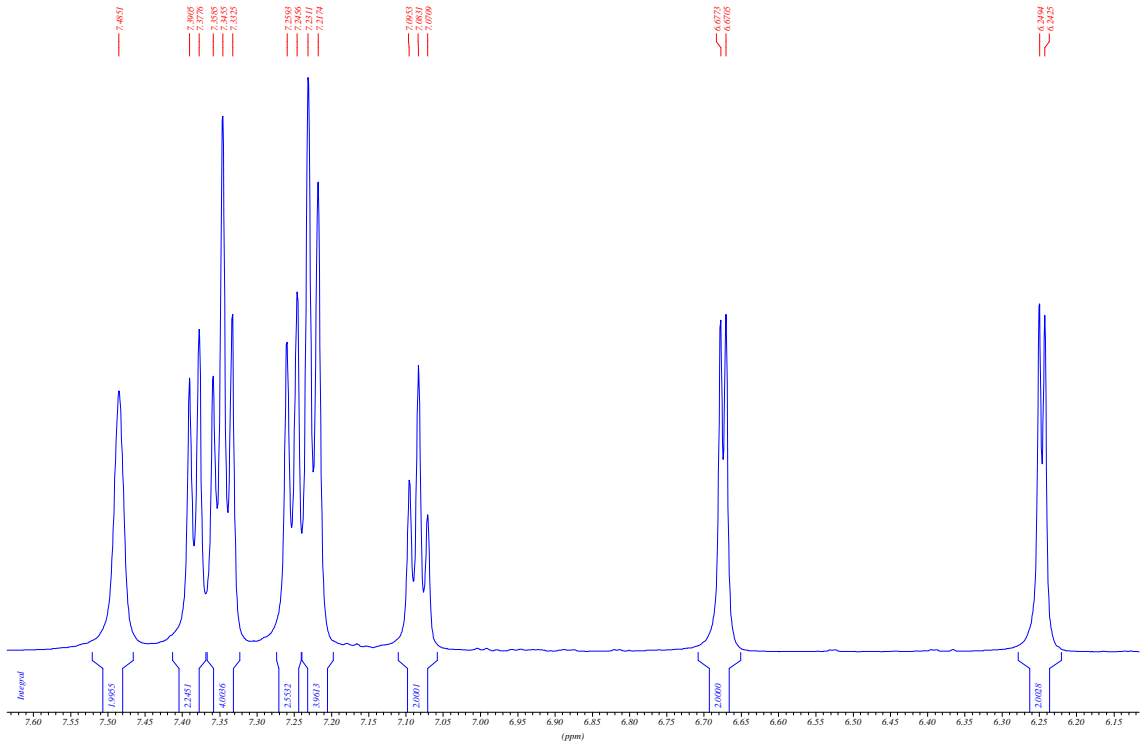
↑ **Figure S5.** Plots of (a) the absorption maxima $\bar{\nu}_{abs}$ and (b) fluorescence emission maxima $\bar{\nu}_{em}$ for compound **1** versus $f(n^2) = (n^2 - 1)/(2n^2 + 1)$ for the solvents of Table 2. The straight lines represent the best fits to the data (for $\bar{\nu}_{abs}$: $r = 0.957$; for $\bar{\nu}_{em}$: $r = 0.938$).



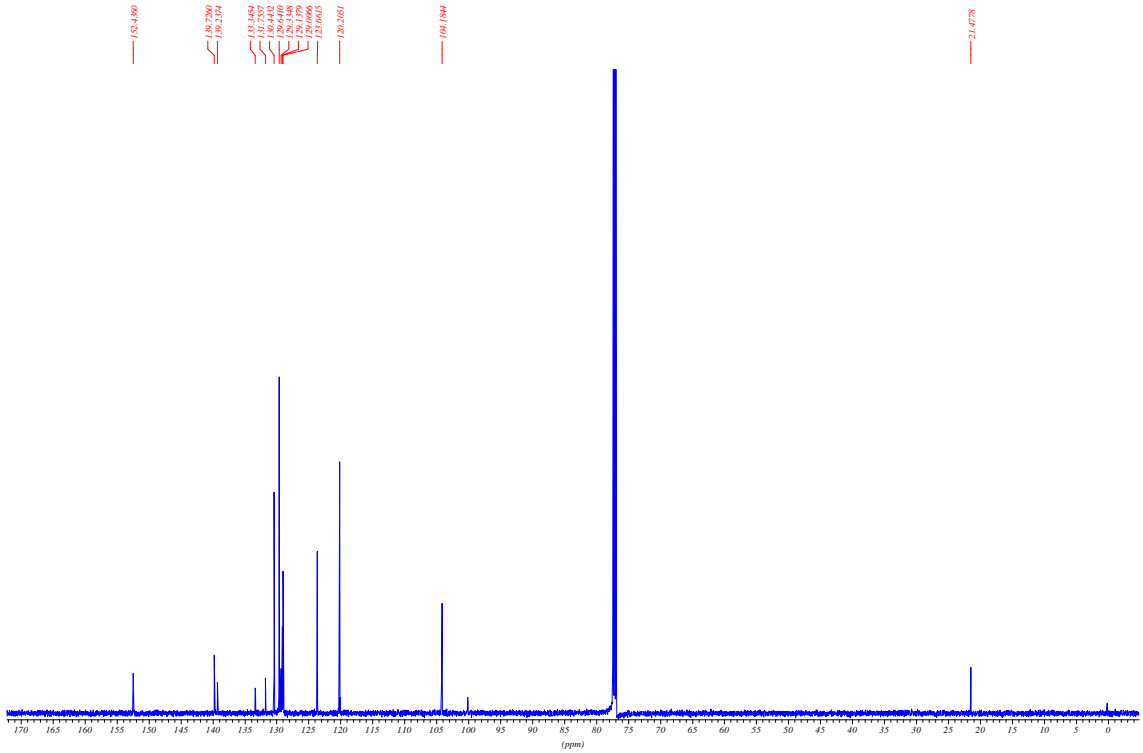
↑ **Figure S6.** Plot of k_{nr} for compound **1** versus SdP for the solvents of Table 2. The straight line represents the best fit to the data ($r = 0.709$).



↑ **Figure S7.** 600 MHz ^{1}H NMR spectrum of compound **1** in $CDCl_3$.



↑ **Figure S8.** 600 MHz ^{1}H NMR spectrum (detail) of compound **1** in $CDCl_3$.



↑ **Figure S9.** 150 MHz ^{13}C NMR spectrum of compound **1** in $CDCl_3$.