

# Combined Effects of Ion-Pairing on Multi-Emissive Properties of Benzimidazolium Salts

Gabriele Di Carlo,<sup>\*[a]</sup> Alessandra Forni,<sup>\*[b]</sup> Paola Moretti,<sup>[a]</sup> Daniele Marinotto,<sup>[b]</sup> Chiara Botta,<sup>[c]</sup> Maddalena Pizzotti,<sup>[a]</sup> Francesca Tessore<sup>[a]</sup> and Elena Cariati<sup>[a]</sup>

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[a] Prof. E. Cariati, Prof. F. Tessore, Prof. M. Pizzotti, Dr. G. Di Carlo and Mrs. P. Moretti

Department of Chemistry  
University of Milan and INSTM Research Unit  
Via C. Golgi 19, 20133 Milan (Italy)  
E-mail: [gabriele.dicarlo@unimi.it](mailto:gabriele.dicarlo@unimi.it)

[b] Dr. A. Forni and Dr. D. Marinotto  
CNR-SCITEC, Istituto di Scienze e Tecnologie Chimiche "G. Natta"  
Via C. Golgi 19, 20133 Milan (Italy)  
E-mail: [alessandra.forni@scitec.cnr.it](mailto:alessandra.forni@scitec.cnr.it)

[c] Dr. Chiara Botta  
CNR-SCITEC, Istituto di Scienze e Tecnologie Chimiche "G. Natta"  
Via A. Corti 12, 20133 MILANO (Italy)

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# 1 Experimental details

## 1.1 General information

All reagents and solvents involved in the synthesis were purchased from Sigma Aldrich and used as received, except THF (freshly distilled from Na/benzophenone under nitrogen atmosphere). Glassware has been flame-dried under vacuum before use when necessary.  $^1\text{H}$ -NMR spectra were recorded on a Bruker Avance DRX-400 in  $\text{DMSO-}d_6$ ,  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$  as solvents at  $10^{-3}\text{M}$  ( $10^{-5}\text{M}$  where shown). Elemental analysis was carried out with a Perkin-Elmer CHN 2400 instrument.

## 1.2 Synthesis

Triflate (**1-OTf**), nitrate (**1-NO<sub>3</sub>**) and iodide (**1-I**) salts of 1,3-dimethyl-2-(4-methylphenyl)-1H-benzimidazolium (**1**) are easily obtained by following the synthetic strategy previously reported by some of us.[S1] The high purity grade of the final products, required for photophysical measurements, are obtained by Biotage flash chromatography and multiple recrystallizations with proper solvents.

**1-OTf crystals** were obtained by repeated crystallization steps from ethanol at +4°C. Elemental analysis calcd (%) for  $\text{C}_{17}\text{H}_{17}\text{F}_3\text{N}_2\text{O}_3\text{S}$ : C 52.84, H 4.43, N 7.25; found C 52.71, H 4.43, N 7.24. MS-ESI (+) m/z: calcd (%) for  $\text{C}_{16}\text{H}_{17}\text{N}_2^+$  237, found 237  $[\text{M}]^+$ . MS-ESI (-) m/z: calcd (%) for  $\text{CF}_3\text{O}_3\text{S}^-$  149, found 149  $[\text{M}]^-$ .

**1-NO<sub>3</sub>·0.5EtOH crystals** were obtained by repeated crystallization steps from ethanol at +4°C. Elemental analysis calcd (%) for  $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_3$ : C 63.34, H 6.25, N 13.04; found C 63.18, H 6.23, N 13.08. MS-ESI (+) m/z: calcd (%) for  $\text{C}_{16}\text{H}_{17}\text{N}_2^+$  237, found 237  $[\text{M}]^+$ . MS-ESI (-) m/z: calcd (%) for  $\text{NO}_3^-$  62, found 62  $[\text{M}]^-$ .

**1-NO<sub>3</sub>·H<sub>2</sub>O crystals** were obtained by repeated crystallization steps from acetonitrile/water (9:1) solution at +4°C. Elemental analysis calcd (%) for  $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_4\cdot[0.5\text{C}_2\text{H}_6\text{O}]$ : C 60.56, H 6.03, N 13.24; found C 60.47, H 6.01, N 13.21. MS-ESI (+) m/z: calcd (%) for  $\text{C}_{16}\text{H}_{17}\text{N}_2^+$  237, found 237  $[\text{M}]^+$ . MS-ESI (-) m/z: calcd (%) for  $\text{NO}_3^-$  62, found 62  $[\text{M}]^-$ .

**1-I·0.5CH<sub>2</sub>Cl<sub>2</sub> crystals** were obtained by repeated crystallization steps from dichloromethane at +4°C. Elemental analysis calcd (%) for  $\text{C}_{16}\text{H}_{17}\text{IN}_2\cdot[0.5\text{CH}_2\text{Cl}_2]$ : C 48.73, H 4.46, N 6.89; found C 48.87, H 4.46, N 6.90. MS-ESI (+) m/z: calcd (%) for  $\text{C}_{16}\text{H}_{17}\text{N}_2^+$  237, found 237  $[\text{M}]^+$ . MS-ESI (-) m/z: calcd (%) for  $\text{I}^-$  127, found 127  $[\text{M}]^-$ .

## 1.3 Single crystal X-ray crystallographic studies

X-ray data of **1-OTf**, **1-NO<sub>3</sub>·0.5EtOH**, **1-NO<sub>3</sub>·H<sub>2</sub>O** and **1-I·0.5CH<sub>2</sub>Cl<sub>2</sub>** were collected on a Bruker Apex II diffractometer using  $\text{MoK}\alpha$  radiation. The structures were solved using direct methods and refined using a full-matrix least squares procedure based on  $F^2$  using all data [S2]. Hydrogen atoms were

placed at geometrically estimated positions. Details relating to the crystals and the structural refinements are presented in Table S2. Full details of crystal data and structure refinement, in CIF format, are available as Supplementary Information.

CCDC reference numbers: 2018732 (**1-OTf**), 2018733 (**1-NO<sub>3</sub>·0.5EtOH**), 2018734 (**1-NO<sub>3</sub>·H<sub>2</sub>O**) and 2018735 (**1-I·0.5CH<sub>2</sub>Cl<sub>2</sub>**).

#### 1.4 Computational details

DFT and TDDFT calculations have been performed in vacuo at the  $\omega$ B97X/6-311++G(d,p) level of theory on both the 1,3-dimethyl-2-(4-methylphenyl)-1H-benzimidazolium cation **1** and its salts with OTf<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and I<sup>-</sup> anions. The  $\omega$ B97X [S3] functional was used owing to its ability in correctly treating at the same time not only ground and excited states properties, but also intermolecular interactions. In the case of the free cation, geometry was fully optimized starting from the X-ray one of **1-OTf**. As for the salts, the cation-anion pairs displaying the shortest intermolecular contacts in the corresponding X-ray structures have been extracted from the crystal and submitted to geometry optimization by constraining angles and torsions to the experimental values.

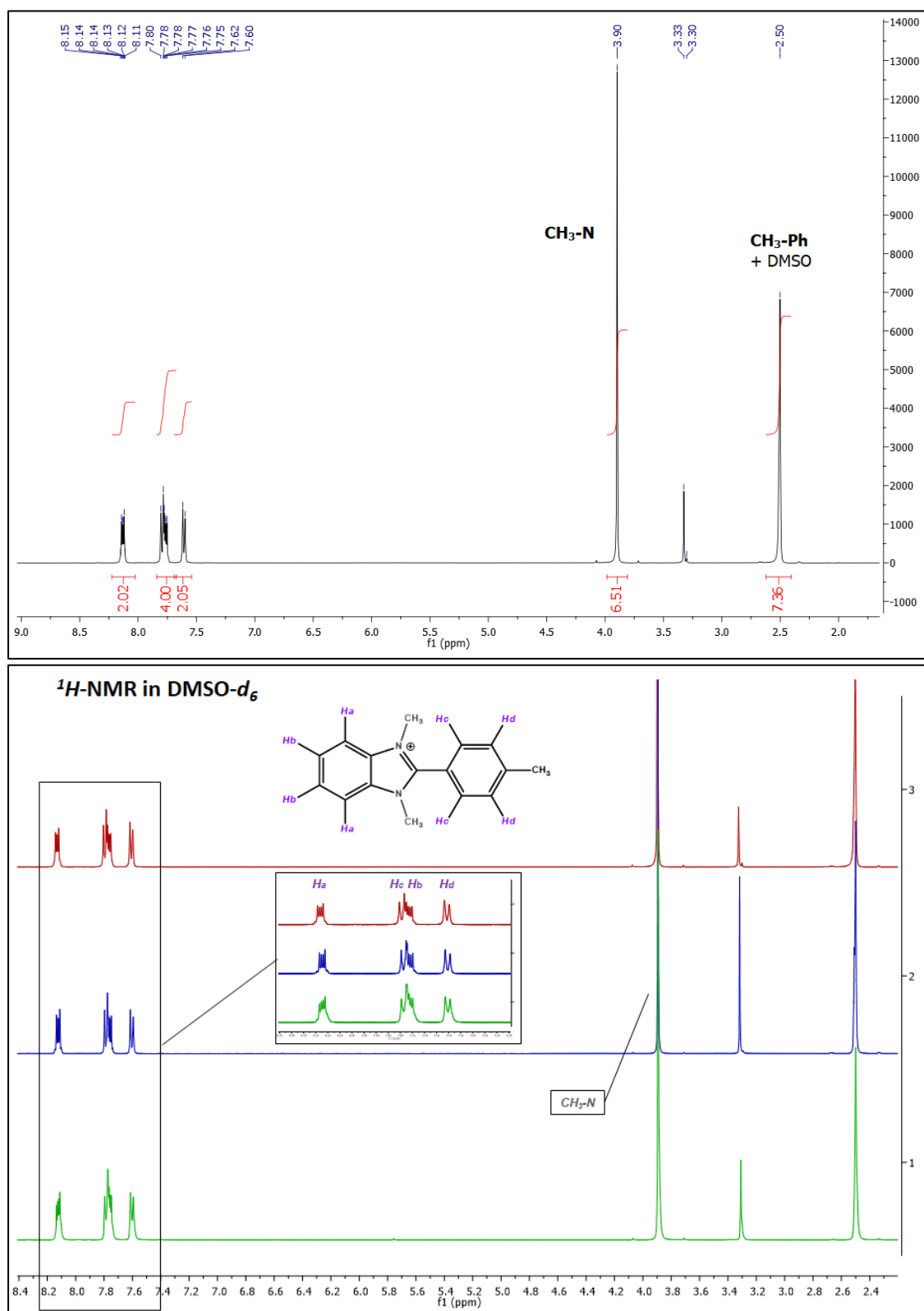
All calculations have been performed with the Gaussian 16 program (Revision A.03) [S4].

#### 1.5 Photophysical characterization

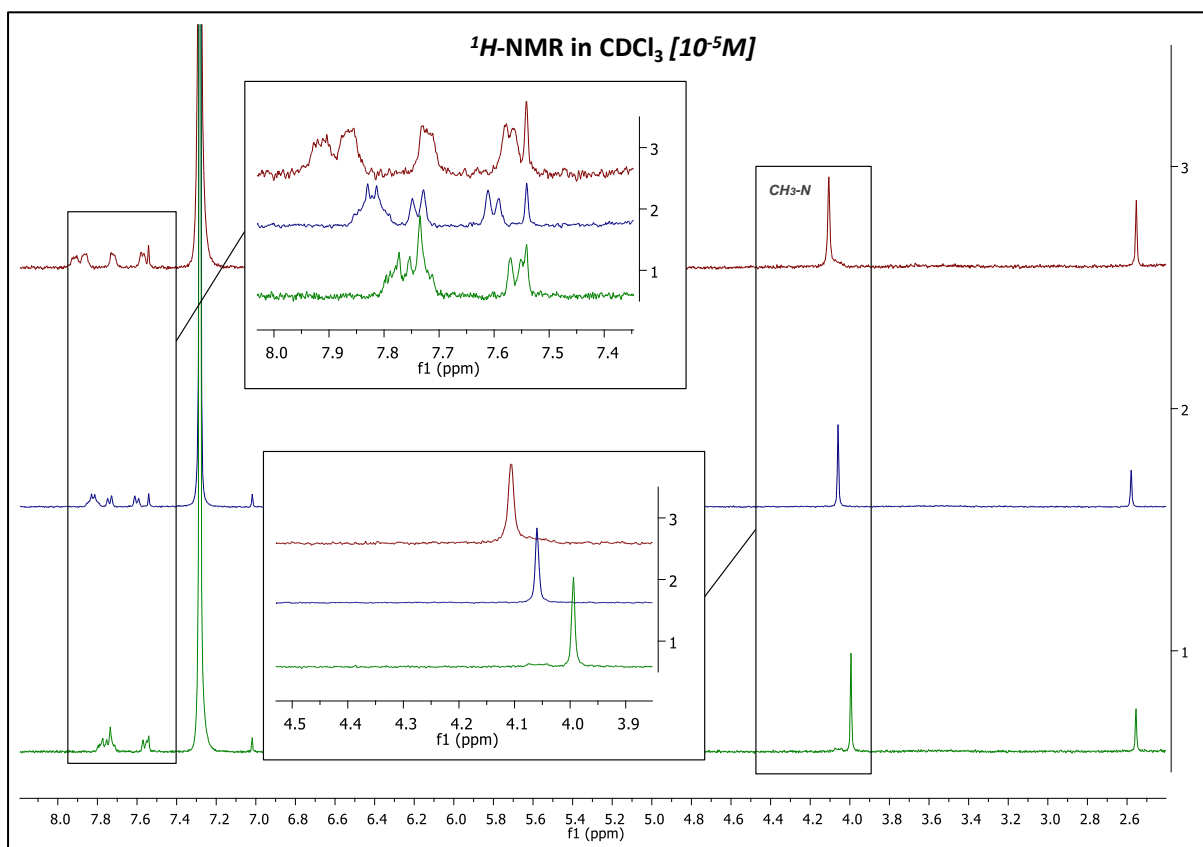
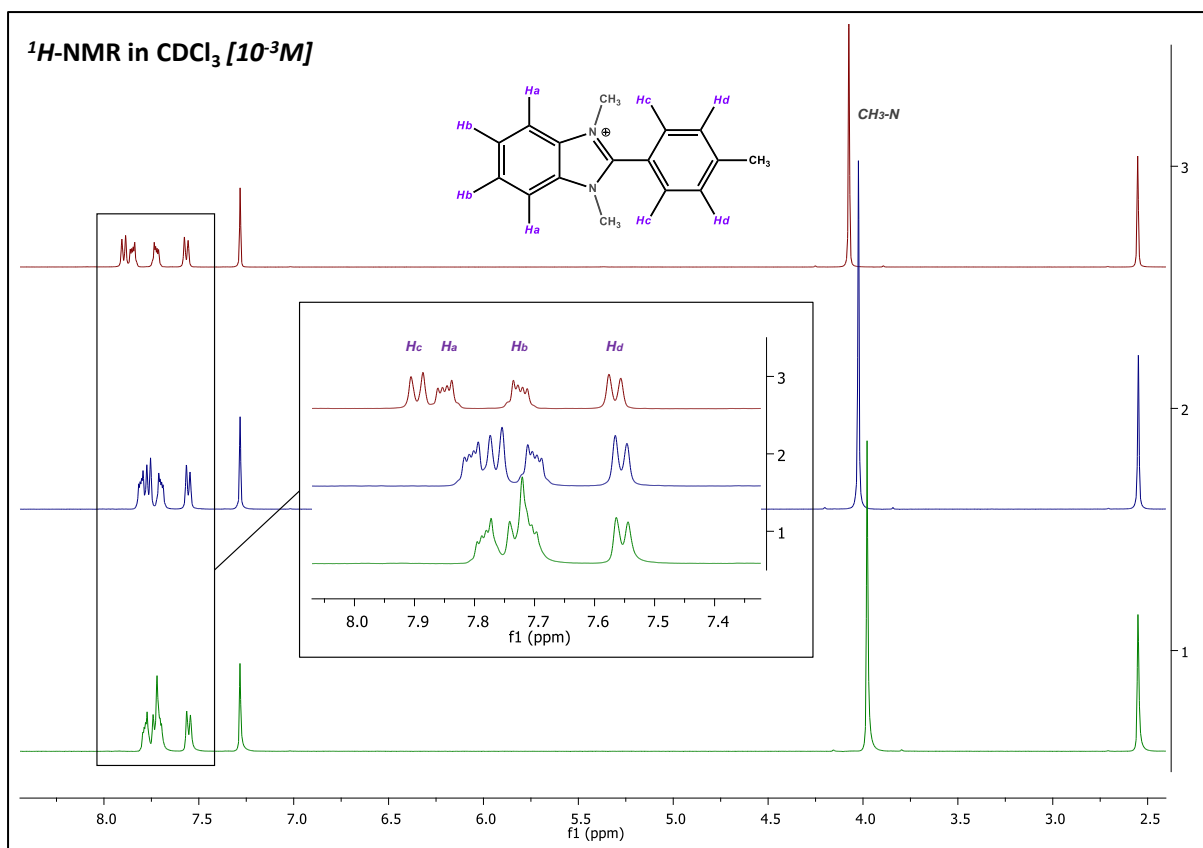
Luminescence measurements. Steady state emission and excitation spectra and photoluminescence lifetimes were obtained using a FLS 980 spectrofluorimeter (Edinburgh Instrument Ltd). The steady state measurements were obtained by a 450 W Xenon arc lamp. Photoluminescence lifetime measurements were performed using: Edinburgh EPLED-300, (Edinburgh Instrument Ltd) and microsecond flash Xe-lamp (60W, 0.1÷100 Hz) with data acquisition devices time correlated single-photon counting (TCSPC) and multi-channel scaling (MCS) methods, respectively.

Photoluminescence quantum yields were measured using a C11347 Quantaaurus – Absolute Photoluminescence Quantum Yield Spectrometer (Hamamatsu Photonics K.K), equipped with a 150 W Xenon lamp, an integrating sphere and a multichannel detector.

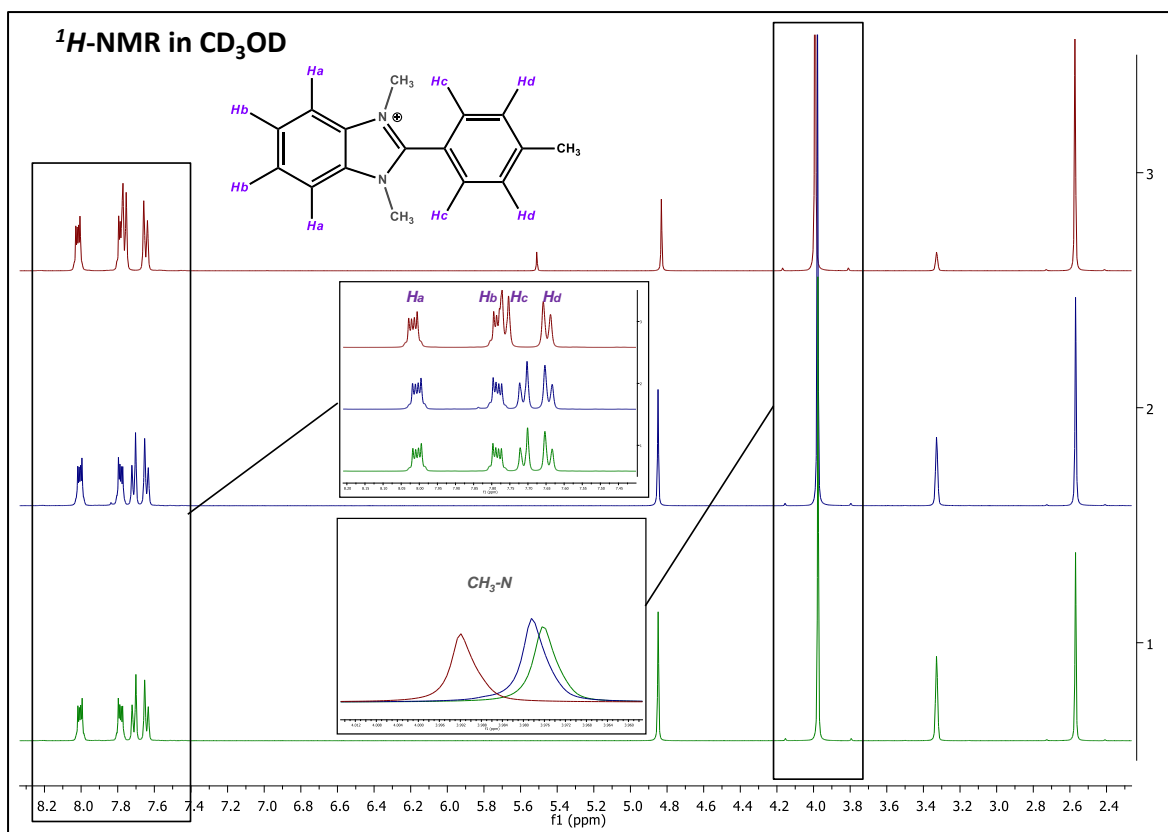
## 2 NMR studies



**Figure S1:** Integrated  $^1\text{H-NMR}$  spectrum (up) of **1-I** (at 298K) in  $\text{DMSO-}d_6$ . Stacked  $^1\text{H-NMR}$  spectra (down) of **1-I** (red); **1-NO<sub>3</sub>** (blue); **1-OTf** (green).



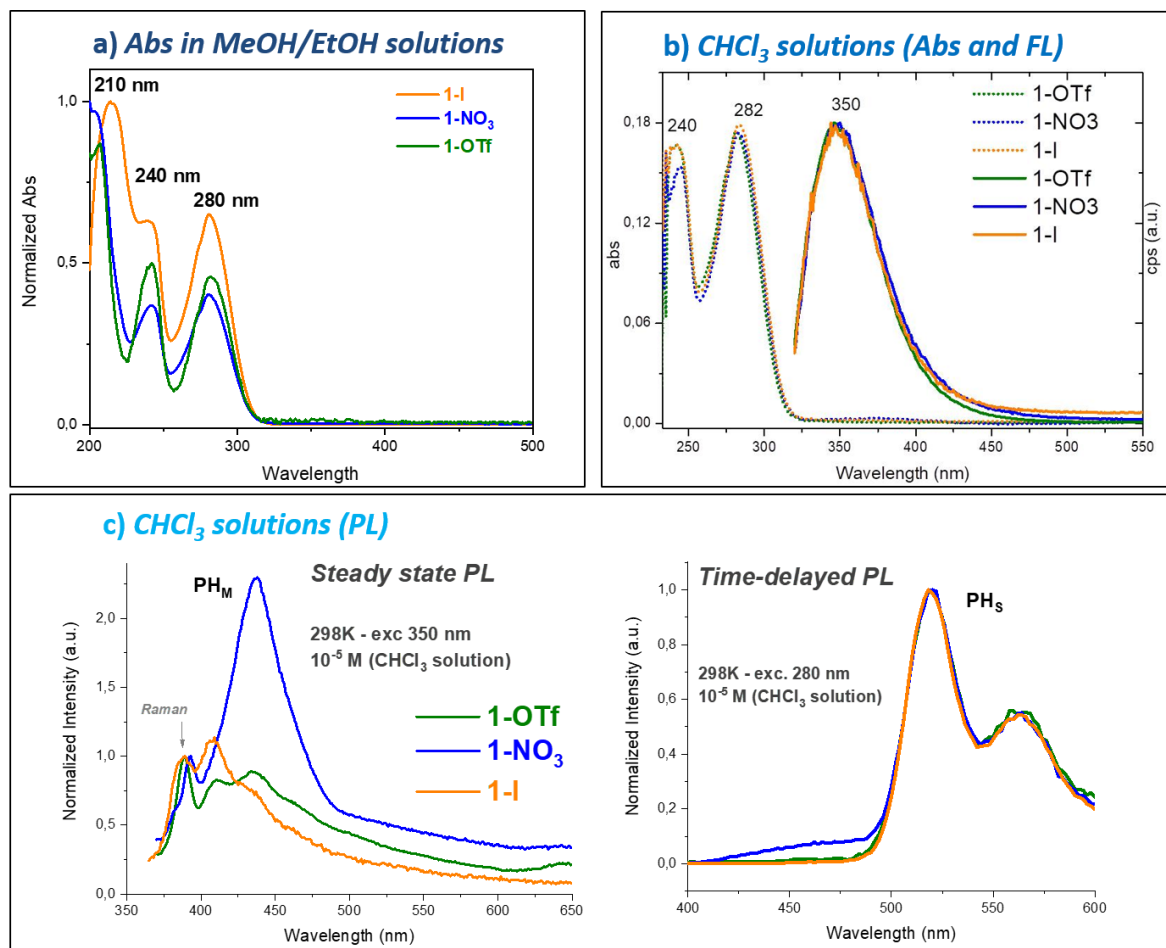
**Figure S2.** Stacked  $^1\text{H-NMR}$  spectra (at 298K) in  $\text{CDCl}_3$  of **1-I** (red); **1-NO<sub>3</sub>** (blue); **1-OTf** (green):  $10^{-3}\text{M}$  up;  $10^{-5}\text{M}$  down.



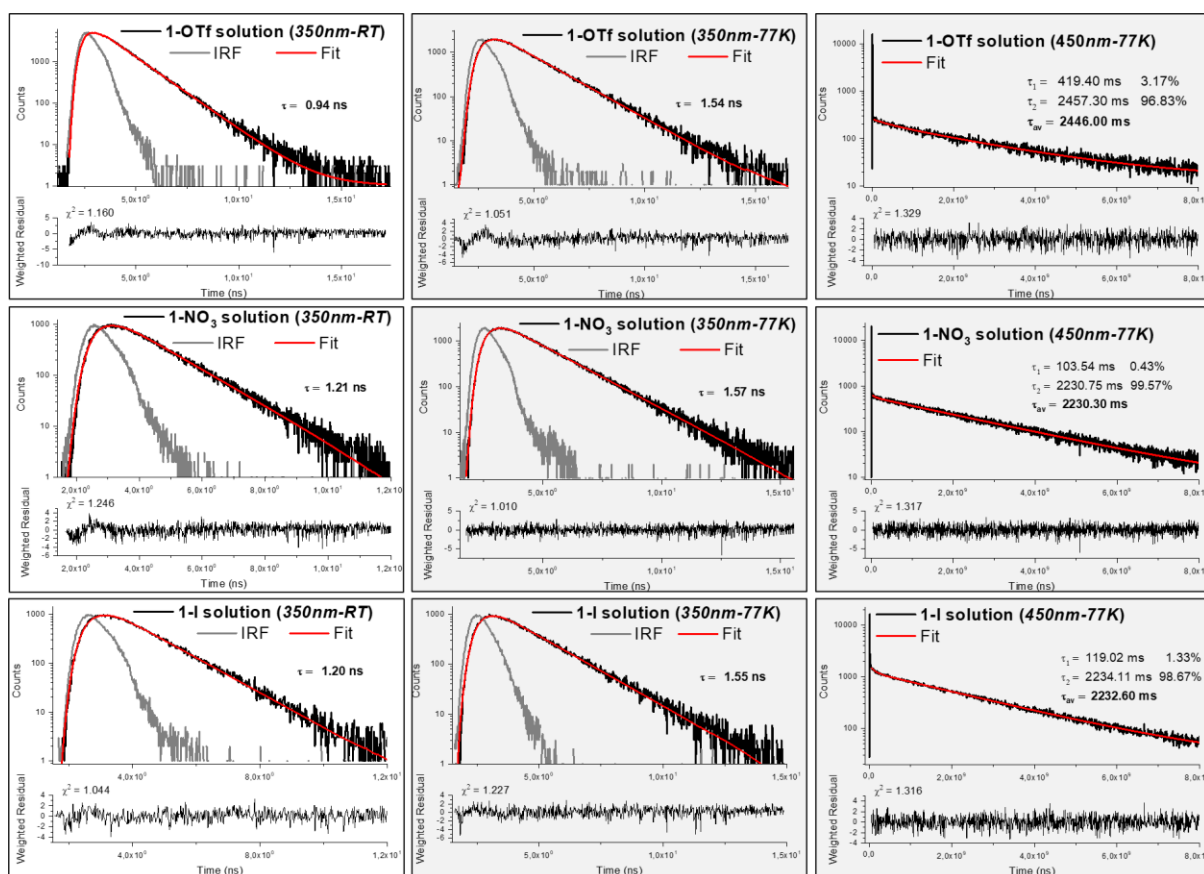
**Figure S3.** Stacked <sup>1</sup>H-NMR spectra (at 298K) in CD<sub>3</sub>OD of **1-I** (red); **1-NO<sub>3</sub>** (blue); **1-OTf** (green).

### 3 Photophysical Studies

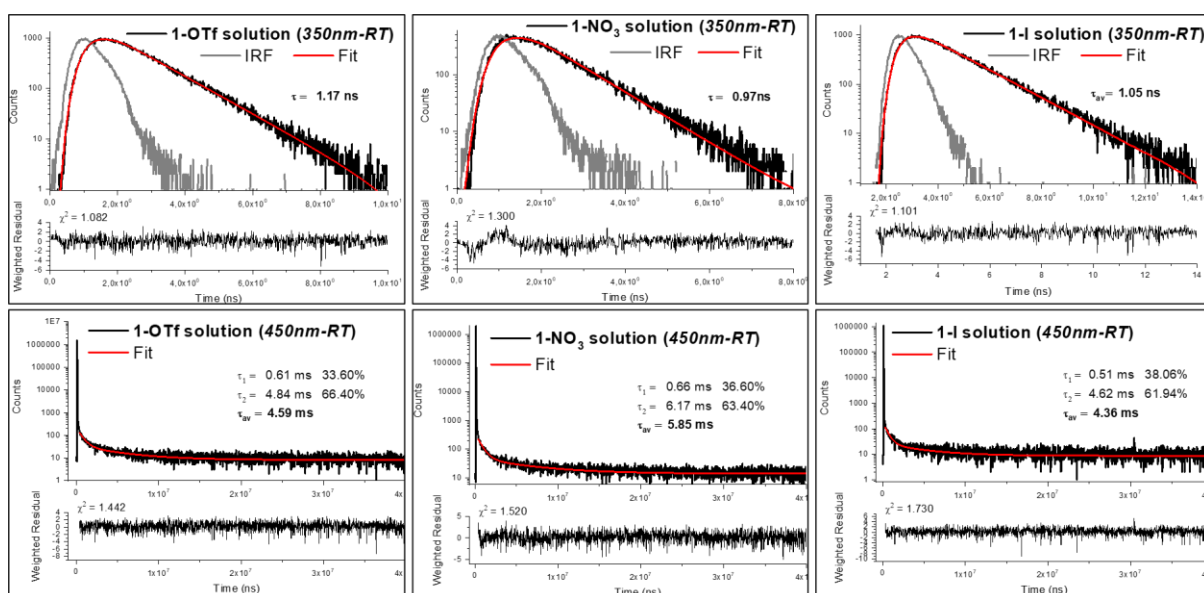
#### 3.1 Solutions



**Figure S4.** a) Absorption spectrum of diluted solutions ( $10^{-5}$  M) of **1**-salts in MeOH/EtOH. b) Absorption (solid line) and emission spectra (dotted line; exc 300 nm) at RT of diluted solutions ( $10^{-5}$  M) of **1**-salts in CHCl<sub>3</sub>. c) Steady-state and time-delayed PL emission spectra of **1**-salts in CHCl<sub>3</sub> (delay time 0.2 ms and window 1.5 ms for **1-OTf** and **1-I**; delay time 0.1 ms and window 0.5 ms for **1-NO<sub>3</sub>**).



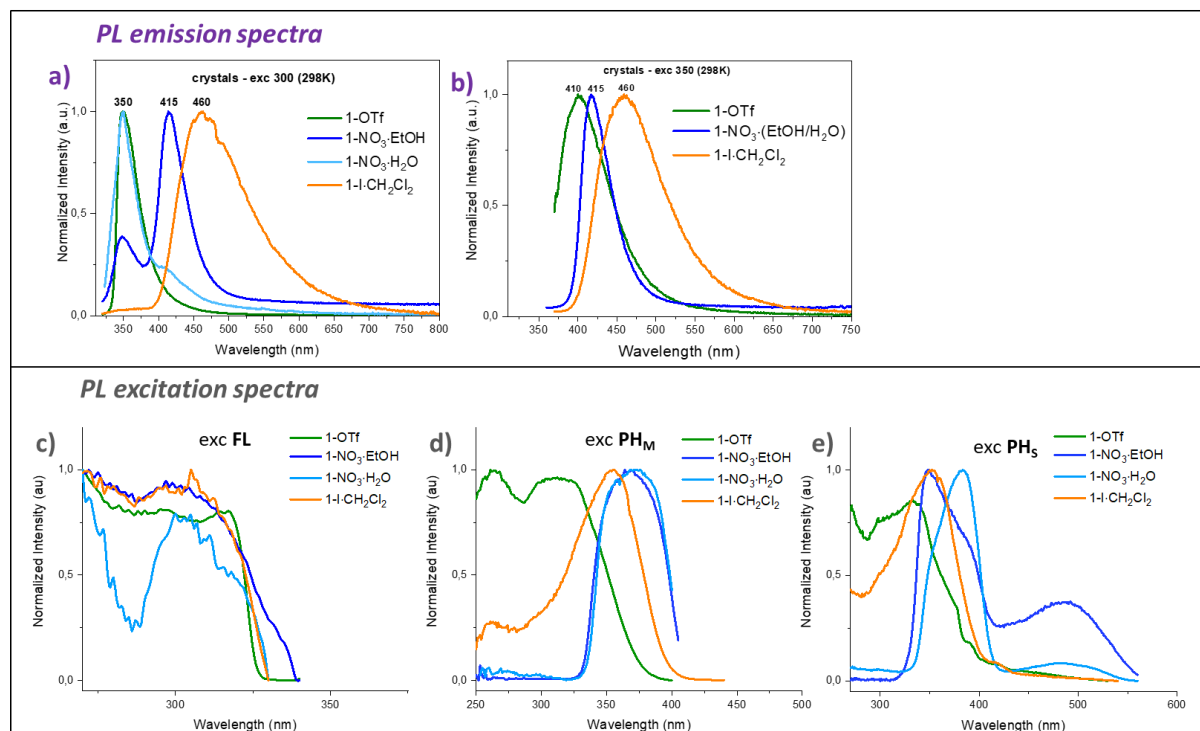
**Figure S5:** Emission decay profiles of 1-salts (excitation 300 nm) in MeOH/EtOH (1:4) diluted solution ( $10^{-5}$  M) at 298K and 77K.



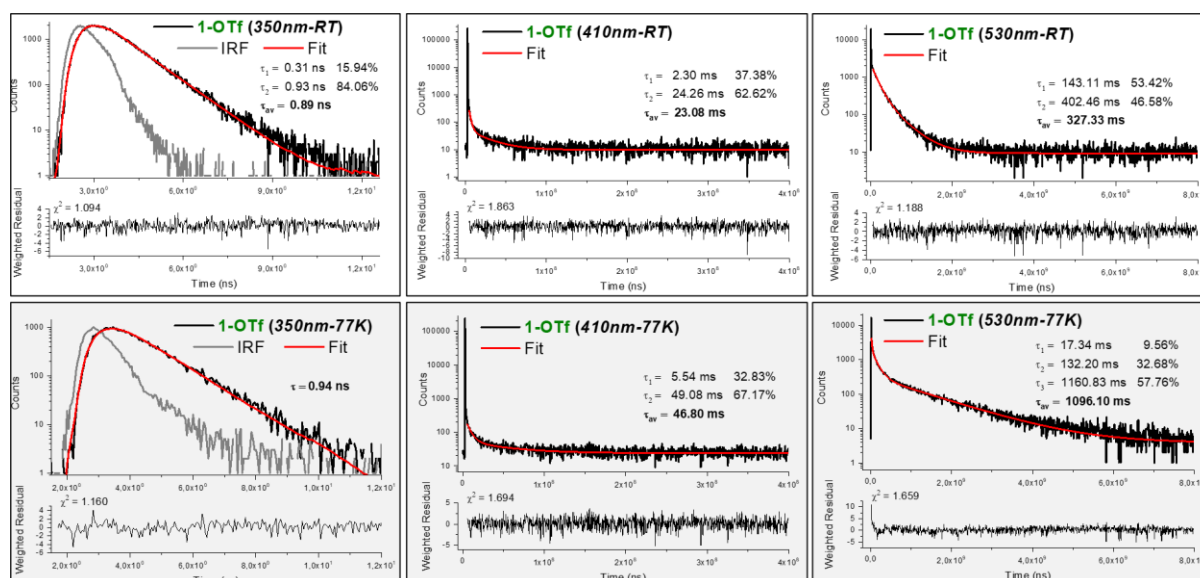
**Figure S6:** Emission decay profiles of 1-salts (excitation 300 nm) in non-polar solvent ( $10^{-5}$  M in CHCl<sub>3</sub>) at 298K.



## 3.2 Solids



**Figure S7.** a) PL emission spectra of **1-OTf**, **1-NO<sub>3</sub>·EtOH**, **1-NO<sub>3</sub>·H<sub>2</sub>O** and **1-I·CH<sub>2</sub>Cl<sub>2</sub>** crystals at 298K (300 nm excitation). b) PL emission spectra at 298K under 350 nm excitation. c) Fluorescence excitation spectra. d) Molecular Phosphorescence excitation spectra. e) Supramolecular Phosphorescence excitation spectra.



**Figure S8.** FL (350 nm), PH<sub>M</sub> (410 nm) and PH<sub>S</sub> (530 nm) decay profiles of **1-OTf** crystals (excitation 300 nm).

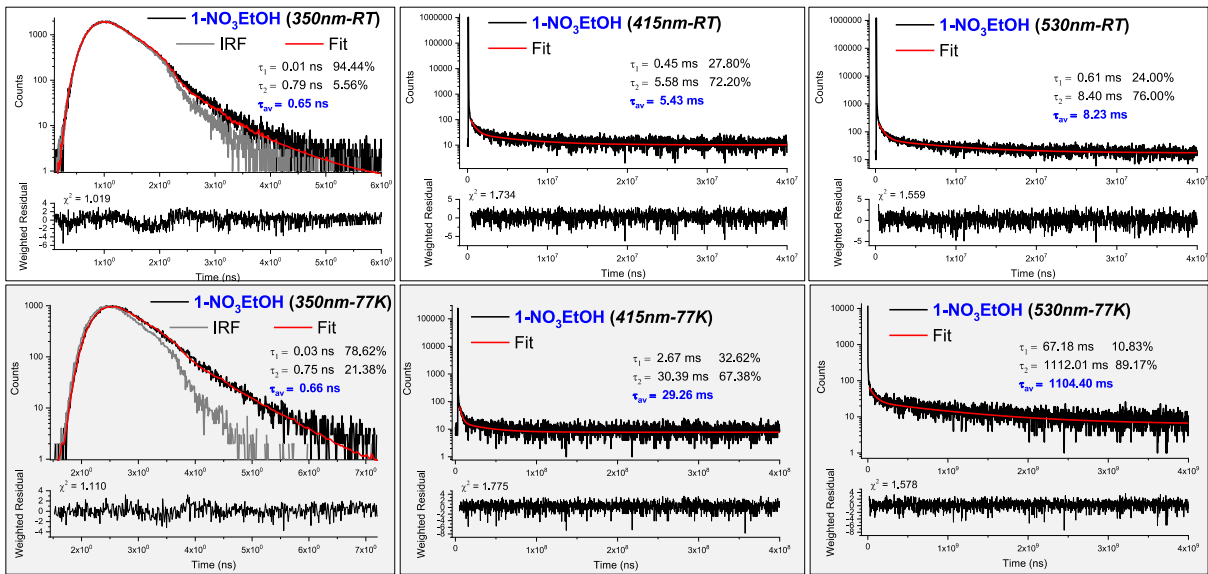


Figure S9. FL (350 nm),  $\text{PH}_M$  (415 nm) and  $\text{PH}_S$  (530 nm) decay profiles of  $1\text{-NO}_3\text{-EtOH}$  crystals (excitation 300 nm).

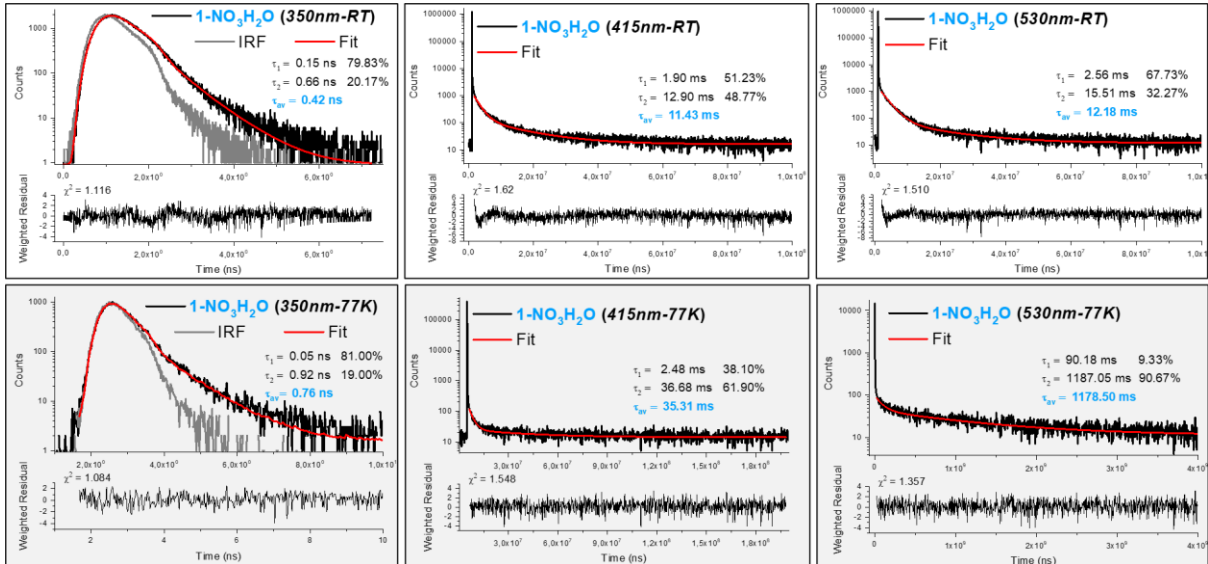
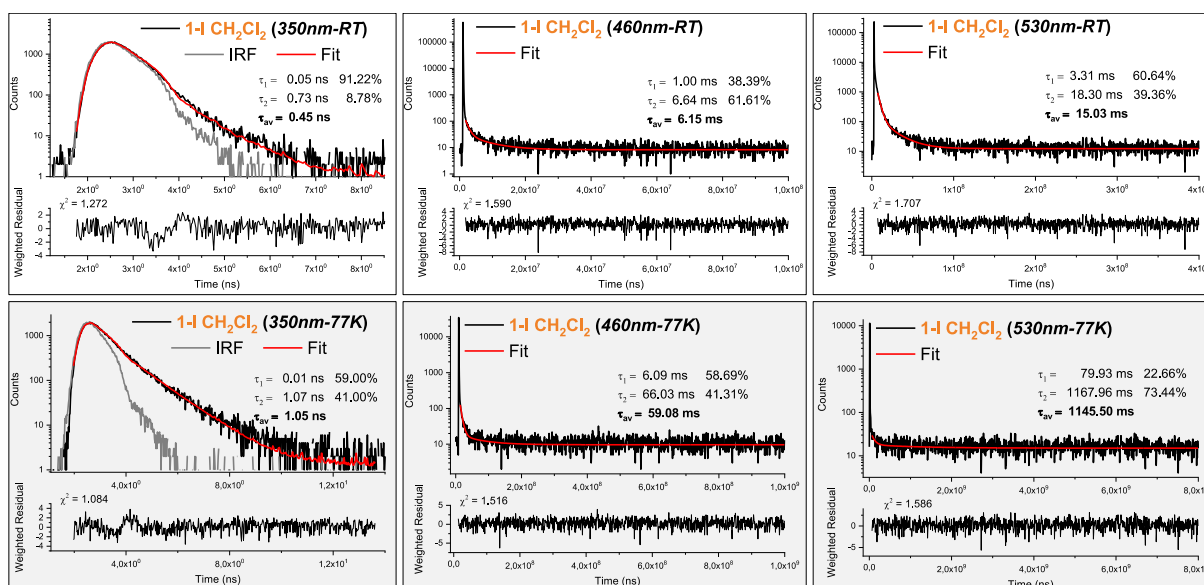


Figure S10. FL (350 nm),  $\text{PH}_M$  (415 nm) and  $\text{PH}_S$  (530 nm) decay profiles of  $1\text{-NO}_3\text{-H}_2\text{O}$  crystals (excitation 300 nm).



**Figure S11.** FL (350 nm), PH<sub>M</sub> (460 nm) and PH<sub>S</sub> (530 nm) decay profiles of **1-I·CH<sub>2</sub>Cl<sub>2</sub>** crystals (excitation 300 nm).

**Table S1.** Radiative ( $K_r$ ) and non-radiative ( $K_{nr}$ ) constants of **1**-salts.

		$\phi$	$\tau$ (ns)	$K_r$ (s <sup>-1</sup> ) <sup>a</sup>	$K_{nr}$ (s <sup>-1</sup> ) <sup>b</sup>	$K_r/K_{nr}$
<b>1-Otf</b> MeOH/EtOH	<i>Em</i> 350 (exc300)	0,775	0,94	<b>8,24E+08</b>	<b>2,39E+08</b>	<b>3,45</b>
	<b>1-Otf</b> crystal	<i>Em</i> 350 (exc300)	0,507	0,89	<b>5,69E+08</b>	<b>5,54E+08</b>
	<i>Em</i> 410 (exc350)	0,347	2,3E+07	<b>15,0870</b>	<b>28,3913</b>	<b>0,53</b>
<b>1-NO<sub>3</sub></b> MeOH/EtOH	<i>Em</i> 350 (exc300)	0,526	1,21	<b>4,35E+08</b>	<b>3,92E+08</b>	<b>1,11</b>
<b>1-NO<sub>3</sub>·EtOH</b> crystal	<i>Em</i> 350 (exc300)	0,037	0,65	<b>5,69E+07</b>	<b>1,48E+09</b>	<b>0,04</b>
	<i>Em</i> 410 (exc350)	0,73	5,4E+06	<b>135,1852</b>	<b>50,0000</b>	<b>2,70</b>
<b>1-NO<sub>3</sub>·H<sub>2</sub>O</b> crystal	<i>Em</i> 350 (exc300)	0,019	0,42	<b>4,52+07</b>	<b>2,34E+09</b>	<b>0,02</b>
	<i>Em</i> 410 (exc350)	0,25	1,14E+07	<b>21,8532</b>	<b>65,5594</b>	<b>0,33</b>
<b>1-I</b> MeOH/EtOH	<i>Em</i> 350 (exc300)	0,536	1,20	<b>4,47E+08</b>	<b>3,87E+08</b>	<b>1,16</b>
<b>1-I·CH<sub>2</sub>Cl<sub>2</sub></b> crystal	<i>Em</i> 350 (exc300)	0,114	0,45	<b>2,53E+08</b>	<b>1,97E+09</b>	<b>0,13</b>
	<i>Em</i> 410 (exc350)	0,237	6,15E+06	<b>38,5366</b>	<b>124,0650</b>	<b>0,31</b>

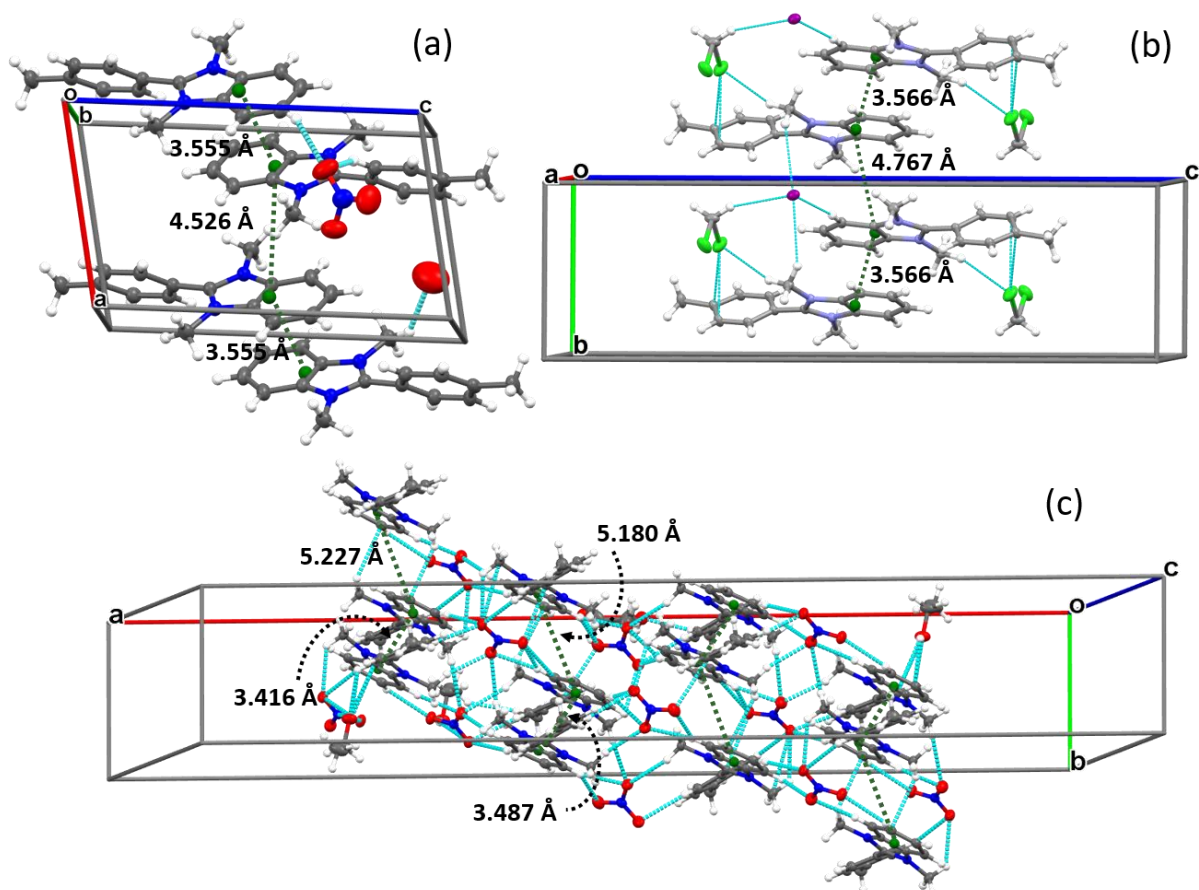
$$^a K_r = \phi \cdot \tau^{-1}$$

$$^b K_{nr} = K_r \cdot (\phi^{-1} - 1)$$

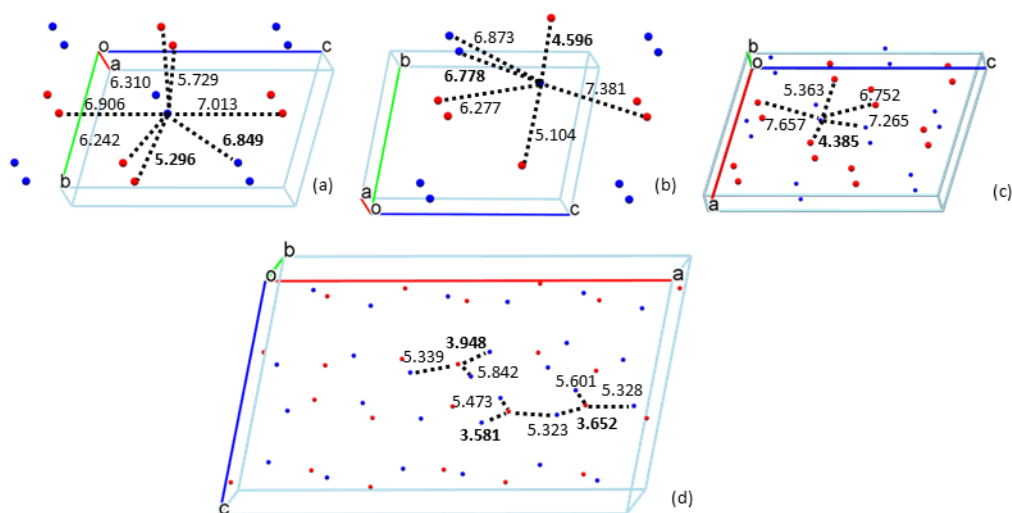
## 4 Crystal structures

**Table S2.** Crystallographic data and structure refinement details for **1-OTf**, **1-NO<sub>3</sub>·0.5EtOH**, **1-NO<sub>3</sub>·H<sub>2</sub>O** and **1-I·0.5CH<sub>2</sub>Cl<sub>2</sub>**

	<b>1-OTf</b>	<b>1-NO<sub>3</sub>·0.5EtOH</b>	<b>1-NO<sub>3</sub>·H<sub>2</sub>O</b>	<b>1-I·0.5CH<sub>2</sub>Cl<sub>2</sub></b>
Chemical Formula	C <sub>16</sub> H <sub>17</sub> N <sub>2</sub> , CF <sub>3</sub> O <sub>3</sub> S	C <sub>16</sub> H <sub>17</sub> N <sub>2</sub> , NO <sub>3</sub> , 0.5(C <sub>2</sub> H <sub>6</sub> O)	C <sub>16</sub> H <sub>17</sub> N <sub>2</sub> , NO <sub>3</sub> , O	2(C <sub>16</sub> H <sub>17</sub> N <sub>2</sub> ), 2I, CH <sub>2</sub> Cl <sub>2</sub>
Molecular weight	386.38	322.36	315.32	813.36
T(K)	293(2)	120(2)	293(2)	120(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>P</i> -1	<i>C</i> 2/ <i>c</i>
a(Å)	7.5128(5)	46.7400(18)	7.456(2)	17.3639(9)
b(Å)	8.6916(5)	7.5898(3)	9.299(3)	7.5370(4)
c(Å)	13.7154(8)	28.5740(11)	12.571(3)	26.8262(14)
α(°)	104.2767(9)	90	75.967(4)	90
β(°)	91.5096(9)	106.8120(10)	77.518(4)	105.8189(7)
γ(°)	91.7180(9)	90	70.952(4)	90
V(Å <sup>3</sup> )	867.02(9)	9703.3(7)	790.3(4)	3377.8(3)
Z	2	24	2	4
D <sub>calcd</sub> (g cm <sup>-3</sup> )	1.480	1.324	1.325	1.599
μ (mm <sup>-1</sup> )	0.237	0.094	0.097	2.048
Crystal size (mm)	0.55 x 0.17 x 0.03	0.32 x 0.33 x 0.22	0.15 x 0.12 x 0.12	0.42 x 0.27 x 0.12
2θ <sub>max</sub> , °	61.04	61.03	61.13	61.02
No. of measured, independent and observed [I > 2σ(I)] reflections	19531 / 5294 / 3976	88189 / 14792 / 10977	14379 / 4815 / 2538	31951 / 5159 / 4935
(R <sub>int</sub> )/(R <sub>σ</sub> )	0.0202 / 0.0190	0.0341 / 0.0267	0.0322 / 0.0404	0.0140 / 0.0093
data/restraints/params	5294 / 0 / 238	14792 / 78 / 690	4811 / 0 / 211	5159 / 0 / 201
R[F <sup>2</sup> > 2σ(F <sup>2</sup> )], wR(F <sup>2</sup> )	0.0695, 0.1278	0.0503, 0.1503	0.0723, 0.2593	0.0187, 0.0482
S	1.055	1.035	1.025	1.067
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.225, -0.355	0.417, -0.243	0.293, -0.432	0.913, -0.627



**Figure S12.** Fragments of crystal packing of (a)  $1\text{-NO}_3\cdot\text{H}_2\text{O}$ , (b)  $1\text{-I}\cdot 0.5\text{CH}_2\text{Cl}_2$  and (c)  $1\text{-NO}_3\cdot 0.5\text{EtOH}$  with contacts shorter than the sum of van der Waals radii (cyan dashed lines) and distances between benzimidazole centroids (green circles). Ellipsoids at 30% ( $1\text{-NO}_3\cdot\text{H}_2\text{O}$ ) and 50% ( $1\text{-I}\cdot 0.5\text{CH}_2\text{Cl}_2$  and  $1\text{-NO}_3\cdot 0.5\text{EtOH}$ ) probability.

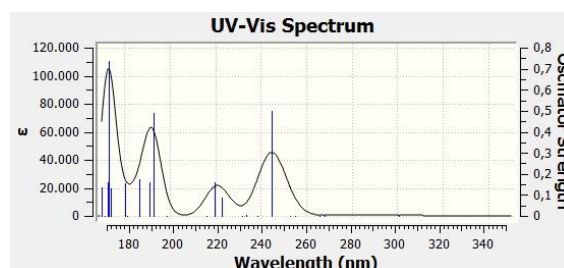


**Figure S13.** Shortest distances between cation and anion (blue and red circles, respectively) centroids in the crystal structures of (a)  $1\text{-OTf}$ , (b)  $1\text{-NO}_3\cdot\text{H}_2\text{O}$ , (c)  $1\text{-I}\cdot 0.5\text{CH}_2\text{Cl}_2$  and (d)  $1\text{-NO}_3\cdot 0.5\text{EtOH}$ .

## 5 Theoretical studies

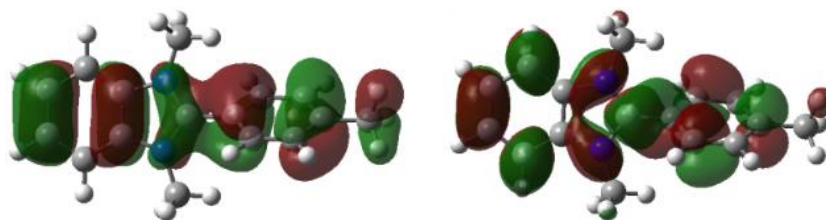
Comparison between the optimized geometry of **1** in gas phase with the X-ray ones of the **1-OTf**, **1-NO<sub>3</sub>·0.5EtOH**, **1-NO<sub>3</sub>·H<sub>2</sub>O** and **1-I·0.5CH<sub>2</sub>Cl<sub>2</sub>** salts indicates that crystal packing does not perturb significantly the molecular conformation, which can be then supposed to be preserved also in solution. The optimized structure of **1** is in fact only slightly more twisted with respect to that found in the crystal structures, as indicated by the dihedral angle  $\theta$  between the l.s. planes through the benzimidazole moiety and the phenyl atoms. This angle measures in fact 59.92° in the optimized structure of **1** and 52.35° in the crystal structure of **1-OTf**, 48.23, 53.21 and 49.71° in the three independent molecules of **1-NO<sub>3</sub>·0.5EtOH**, 53.09° in **1-NO<sub>3</sub>·H<sub>2</sub>O** and 48.33° in **1-I·0.5CH<sub>2</sub>Cl<sub>2</sub>**. Moreover, the distance of the C9–C10 bond connecting the two aromatic moieties is comparable in all cases, varying from 1.462 to 1.469 Å, suggesting a similar conjugation degree in the isolated cation and in the salts.

The simulated absorption spectrum of **1** is reported in Figure S14 (see Table S3 for the first singlet and triplet excitation energies). The overall shape of the spectrum reproduces the experimental one in MeOH/EtOH (displaying three bands at 210, 240 and 280 nm), though the computed maxima (at 190, 220, 245 nm) are slightly shifted towards higher energies.



**Figure S14.**  $\omega$ B97X/6-311++G(d,p) computed absorption spectrum of **1**, resulting from convolution of the excitation energies (blue sticks) with 0.15 eV of half-bandwidth

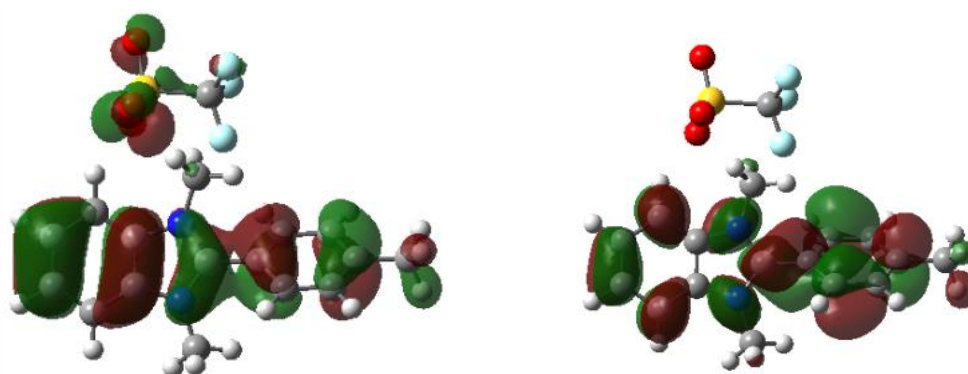
The  $S_0 \rightarrow S_1$  excitation, computed at 245 nm with oscillator strength  $f=0.60$ , is mainly (75%) a HOMO  $\rightarrow$  LUMO transition where both HOMO and LUMO are  $\pi$  orbitals delocalized on the whole molecule (see Figure S15).



**Figure S15.** Plot of  $\omega$ B97X/6-311++G(d,p) HOMO (left) and LUMO (right) of the optimized geometry of **1** with an isosurface value of 0.02.

Analysis of the first singlet and triplet excitation energies (see Table S3) reveals the presence of a triplet state ( $T_7$ ) of  $(\pi, \pi^*)$  character just below  $S_1$  ( $\Delta E=0.162$  eV, 8 nm). Such small S-T energy gap could allow an otherwise forbidden ISC from the singlet to the close triplet state which decays to  $T_1$  by internal conversion, explaining the fluorescent (from  $S_1$ ) and phosphorescent (from  $T_1$ ) emission of solutions of **1**-salts, the latter observed only at low temperature, as usually happen for typical organic molecules. The  $(\pi, \pi^*)$  character of the emission from  $T_1$  to  $S_0$  explains its long lifetimes in solution.

Calculations of the excitation energies on the **1-OTf**, **1-NO<sub>3</sub>** and **1-I** ionic pairs to simulate any effect of the counterion on the emissive properties of **1** (see Table S4 for **1-OTf**) provide the first significantly populated (i.e. with  $f>0.1$ ) singlet excited state slightly shifted towards lower energies (248, 249 and 253 nm for **1-OTf**, **1-NO<sub>3</sub>** and **1-I**, respectively) with respect to **1**. Moreover, they display CT character from the anion towards **1** as exemplified in Figure S16 for **1-OTf**, where we plot the MOs mainly involved (66%) in the  $S_0 \rightarrow S_1$  transition.

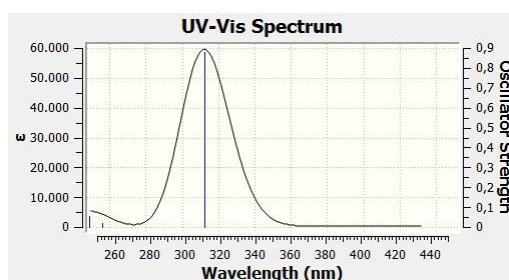


**Figure S16.** Plot of  $\omega$ B97X/6-311++G(d,p) occupied (left) and unoccupied (right) MOs mainly involved in the  $S_0 \rightarrow S_1$  transition of the **1-OTf** pair (isosurface value 0.02).

Optimization of  $S_1$  of **1** (see Figure S17 for the simulated spectrum of fluorescence) leads to a more planar conformation with respect to the ground state one (the dihedral angle  $\theta$  measures  $27.77^\circ$ ),



indicating a larger conjugation within the molecule. In fact, the C–C bond connecting the phenyl ring with benzimidazole shortens from 1.469 (ground state) to 1.402 Å (excited state). The fluorescence is computed at 312 nm with high oscillator strength ( $f=0.88$ ), in agreement with the high quantum yields measured in solution. The computed Stokes shift (about 70 nm) is comparable with the experimental one.



**Figure S17.**  $\omega$ B97X/6-311++G(d,p) fluorescence spectrum of **1**, resulting from convolution of the excitation energies (blue sticks) with 0.2 eV of half-bandwidth

**Table S3.** First TD- $\omega$ B97X/6-311++G(d,p)  $S_0 \rightarrow S_n$  and  $S_0 \rightarrow T_n$  transitions computed on the optimized structure of **1**.

Excitation energies and oscillator strengths:

T1 Excited State	1:	Triplet-A	3.4468 eV	359.71 nm	$f=nd$	$\langle S^{*2} \rangle = 2.000$
	60 -> 64	0.15339				
	60 -> 66	-0.25298				
	61 -> 65	-0.34304				
	61 -> 68	0.10297				
	63 -> 64	0.39109				
	63 -> 66	-0.27116				
T2 Excited State	2:	Triplet-A	3.4953 eV	354.72 nm	$f=nd$	$\langle S^{*2} \rangle = 2.000$
	60 -> 68	-0.19525				
	62 -> 64	0.49892				
	62 -> 66	0.30488				
	62 -> 70	-0.15923				
	63 -> 68	0.19852				
T3 Excited State	3:	Triplet-A	4.1221 eV	300.78 nm	$f=nd$	$\langle S^{*2} \rangle = 2.000$
	60 -> 64	-0.41311				
	60 -> 66	-0.11005				
	61 -> 65	0.15395				
	63 -> 64	0.44410				
	63 -> 66	0.23257				
T4 Excited State	4:	Triplet-A	4.6260 eV	268.02 nm	$f=nd$	$\langle S^{*2} \rangle = 2.000$
	61 -> 64	0.49800				
	61 -> 65	0.11791				
	61 -> 66	-0.42177				
	63 -> 65	-0.10443				
T5 Excited State	5:	Triplet-A	4.6665 eV	265.69 nm	$f=nd$	$\langle S^{*2} \rangle = 2.000$
	60 -> 64	0.27244				
	60 -> 66	-0.10889				
	61 -> 65	0.49220				
	61 -> 66	0.13411				
	61 -> 67	-0.12576				
	61 -> 68	-0.13926				
	63 -> 64	0.16111				



	63 -> 66	-0.24527					
T6 Excited State	6:	Triplet-A	4.8634 eV	254.93 nm	f=nd	<S**2>=2.000	
	59 -> 64	-0.12739					
	60 -> 68	-0.37481					
	62 -> 64	-0.31472					
	63 -> 65	0.20280					
	63 -> 68	0.38059					
T7 Excited State	7:	Triplet-A	4.9040 eV	252.83 nm	f=nd	<S**2>=2.000	
	60 -> 65	0.39016					
	60 -> 67	-0.10349					
	63 -> 65	0.46239					
	63 -> 66	0.11803					
	63 -> 67	-0.10697					
	63 -> 68	-0.21121					
S1 Excited State	8:	Singlet-A	5.0626 eV	244.90 nm	f=0.4991	<S**2>=0.000	
	60 -> 64	-0.15113					
	60 -> 66	-0.18343					
	62 -> 68	-0.20813					
	63 -> 64	0.60912					
T8 Excited State	9:	Triplet-A	5.1996 eV	238.45 nm	f=nd	<S**2>=2.000	
	52 -> 64	-0.10065					
	56 -> 64	0.13488					
	60 -> 66	-0.15474					
	60 -> 70	0.10211					
	62 -> 65	0.15934					
	62 -> 68	0.54527					
	63 -> 70	-0.15433					
	63 -> 72	-0.15996					
S2 Excited State	10:	Singlet-A	5.3058 eV	233.68 nm	f=0.0056	<S**2>=0.000	
	60 -> 65	0.22786					
	61 -> 64	0.41767					
	61 -> 66	-0.31319					
	62 -> 64	0.11152					
	63 -> 65	0.33352					
T9 Excited State	11:	Triplet-A	5.3487 eV	231.80 nm	f=nd	<S**2>=2.000	
	59 -> 64	0.39323					
	59 -> 72	0.12080					
	60 -> 68	-0.15316					
	62 -> 64	0.14717					
	62 -> 66	-0.21286					
	62 -> 70	0.28531					
	62 -> 72	0.26152					
	63 -> 68	0.16861					
S3 Excited State	12:	Singlet-A	5.5616 eV	222.93 nm	f=0.0891	<S**2>=0.000	
	60 -> 68	-0.14616					
	61 -> 64	-0.11434					
	62 -> 64	0.60870					
	62 -> 66	0.19538					
	63 -> 68	0.18833					
S4 Excited State	13:	Singlet-A	5.6397 eV	219.84 nm	f=0.1584	<S**2>=0.000	
	60 -> 64	0.45845					
	61 -> 65	-0.16526					
	62 -> 68	0.26787					
	63 -> 64	0.23038					
	63 -> 66	-0.29816					
T10 Excited State	14:	Triplet-A	5.7372 eV	216.10 nm	f=nd	<S**2>=2.000	
	56 -> 64	-0.15832					
	60 -> 66	0.25802					
	60 -> 70	-0.16405					

60 -> 72	-0.14077					
62 -> 65	0.10545					
62 -> 68	0.34632					
63 -> 66	-0.12914					
63 -> 70	0.27116					
63 -> 72	0.26967					
T11 Excited State 15:	Triplet-A	6.2422 eV	198.62 nm	f=nd	<S**2>=2.000	
52 -> 64	-0.10051					
54 -> 64	-0.11880					
60 -> 64	0.38809					
60 -> 66	0.13123					
60 -> 70	0.18612					
60 -> 72	0.22924					
63 -> 64	0.21992					
63 -> 66	0.30751					
63 -> 72	0.12214					
S5 Excited State 16:	Singlet-A	6.4326 eV	192.74 nm	f=0.4893	<S**2>=0.000	
60 -> 66	0.21409					
61 -> 65	0.40050					
61 -> 66	0.10021					
61 -> 68	-0.13969					
62 -> 65	0.14969					
62 -> 68	0.25670					
63 -> 64	0.16511					
63 -> 66	0.13415					
63 -> 70	0.19251					
63 -> 72	0.20386					
S6 Excited State 17:	Singlet-A	6.4929 eV	190.95 nm	f=0.1580	<S**2>=0.000	
60 -> 65	-0.22664					
61 -> 64	0.49325					
61 -> 72	0.10685					
63 -> 65	-0.37331					

**Table S4** First TD- $\omega$ B97X/6-311++G(d,p)  $S_0 \rightarrow S_n$  and  $S_0 \rightarrow T_n$  transitions computed on 1-OTf.

Excitation energies and oscillator strengths:

Excited State 1:	Triplet-A	3.3598 eV	369.03 nm	f=0.0000	<S**2>=2.000	
91 ->101	0.18923					
91 ->103	-0.11590					
91 ->104	0.21650					
92 ->101	-0.10335					
92 ->102	0.25056					
92 ->103	-0.14444					
95 ->101	0.20504					
95 ->104	-0.13334					
96 ->101	0.34206					
96 ->104	0.10388					
97 ->101	-0.23870					
Excited State 2:	Triplet-A	3.4663 eV	357.68 nm	f=0.0000	<S**2>=2.000	
91 ->101	-0.16279					
92 ->102	-0.15525					
95 ->101	0.37136					
95 ->104	-0.29652					
96 ->101	-0.18054					
96 ->107	-0.12768					
96 ->109	0.14614					
97 ->104	0.14081					
Excited State 3:	Triplet-A	4.1181 eV	301.07 nm	f=0.0000	<S**2>=2.000	
91 ->101	-0.25963					
92 ->101	0.13106					

92 ->102		-0.16702					
92 ->103		0.12427					
96 ->101		0.43211					
96 ->104		-0.27971					
97 ->101		-0.15112					
Excited State	4:	Triplet-A	4.6335 eV	267.58 nm	f=0.0000	<S**2>=2.000	
91 ->101		0.24954					
91 ->104		0.13938					
92 ->101		0.50215					
92 ->102		-0.10276					
92 ->104		0.28730					
96 ->102		0.10285					
Excited State	5:	Triplet-A	4.6867 eV	264.55 nm	f=0.0000	<S**2>=2.000	
91 ->101		-0.28886					
91 ->102		0.17968					
92 ->101		0.16817					
92 ->102		0.39104					
92 ->103		-0.28926					
96 ->104		-0.20212					
Excited State	6:	Triplet-A	4.8200 eV	257.23 nm	f=0.0000	<S**2>=2.000	
90 ->101		-0.20242					
91 ->107		0.13125					
91 ->109		-0.15502					
95 ->101		-0.28257					
96 ->107		-0.28882					
96 ->109		0.31760					
97 ->101		0.15729					
97 ->109		-0.10634					
Excited State	7:	Triplet-A	4.9264 eV	251.67 nm	f=0.0000	<S**2>=2.000	
91 ->102		0.38391					
91 ->103		-0.25085					
92 ->101		-0.15871					
92 ->102		-0.12954					
92 ->103		0.11624					
96 ->102		0.33145					
96 ->103		-0.21979					
97 ->102		-0.15172					
Excited State	8:	Singlet-A	4.9947 eV	248.23 nm	f=0.5335	<S**2>=0.000	
91 ->104		0.13640					
95 ->107		0.12286					
95 ->109		-0.13674					
96 ->101		0.57351					
96 ->104		-0.13447					
97 ->101		-0.24825					
Excited State	9:	Triplet-A	5.1455 eV	240.96 nm	f=0.0000	<S**2>=2.000	
90 ->101		0.14673					
91 ->104		-0.12585					
95 ->104		0.11175					
95 ->107		0.28948					
95 ->109		-0.37317					
96 ->107		-0.14834					
96 ->112		-0.10977					
97 ->109		0.12138					
Excited State	10:	Triplet-A	5.2224 eV	237.41 nm	f=0.0000	<S**2>=2.000	
90 ->101		-0.28695					
91 ->107		-0.10702					
91 ->109		0.12231					
95 ->104		-0.16262					
95 ->107		0.22798					
95 ->109		-0.13795					
95 ->112		0.15429					

95 ->115	0.12239					
96 ->107	0.16035					
96 ->109	-0.20407					
97 ->107	-0.14795					
97 ->109	0.12313					
Excited State 11:	Singlet-A	5.2872 eV	234.50 nm	f=0.0116	<S**2>=0.000	
91 ->101	0.18917					
91 ->102	-0.24992					
91 ->103	0.13838					
92 ->101	0.40203					
92 ->103	-0.11941					
92 ->104	0.21532					
95 ->101	0.14426					
96 ->102	-0.24085					
96 ->103	0.14760					
97 ->102	0.10747					
Excited State 12:	Singlet-A	5.3336 eV	232.46 nm	f=0.0416	<S**2>=0.000	
92 ->101	0.12175					
95 ->101	-0.27256					
95 ->104	0.11105					
97 ->101	0.13443					
100 ->101	0.56197					
100 ->104	-0.10044					
Excited State 13:	Triplet-A	5.3626 eV	231.20 nm	f=0.0000	<S**2>=2.000	
100 ->101	0.68068					
100 ->104	-0.11702					
Excited State 14:	Singlet-A	5.4302 eV	228.32 nm	f=0.0797	<S**2>=0.000	
95 ->101	0.42179					
95 ->104	-0.16085					
96 ->107	-0.10879					
97 ->101	-0.25257					
100 ->101	0.37729					
Excited State 15:	Triplet-A	5.7032 eV	217.39 nm	f=0.0000	<S**2>=2.000	
85 ->101	0.11636					
89 ->101	-0.10825					
91 ->104	-0.18058					
95 ->107	-0.19252					
95 ->109	0.23531					
96 ->104	0.20251					
96 ->110	0.12956					
96 ->111	0.11517					
96 ->112	-0.23044					
96 ->113	-0.10914					
96 ->115	-0.19685					
97 ->107	0.10210					
Excited State 16:	Singlet-A	5.7124 eV	217.04 nm	f=0.1683	<S**2>=0.000	
91 ->101	0.40411					
92 ->101	-0.18264					
92 ->102	0.14325					
95 ->101	-0.13069					
95 ->107	-0.19139					
95 ->109	0.19657					
96 ->101	0.15443					
96 ->104	0.26338					
97 ->104	-0.12323					
Excited State 17:	Singlet-A	6.3707 eV	194.62 nm	f=0.0194	<S**2>=0.000	
90 ->101	-0.12010					
94 ->101	0.10390					
95 ->101	0.22555					
95 ->104	-0.12553					
96 ->101	0.23960					

	97 ->101	0.49976				
	99 ->101	-0.20762				
Excited State	18:	Triplet-A	6.4082 eV	193.48 nm	f=0.0000	<S**2>=2.000
	94 ->101	0.10482				
	95 ->101	0.26622				
	96 ->101	0.19064				
	97 ->101	0.49743				
	97 ->104	-0.14031				
	99 ->101	-0.26866				
Excited State	19:	Singlet-A	6.4092 eV	193.45 nm	f=0.5239	<S**2>=0.000
	91 ->101	0.20984				
	91 ->104	0.14154				
	92 ->101	-0.15968				
	92 ->102	0.32037				
	92 ->103	-0.17073				
	95 ->107	0.21107				
	95 ->109	-0.22290				
	96 ->101	-0.15398				
	96 ->112	0.13113				
	96 ->115	0.11423				
	97 ->101	0.11547				
Excited State	20:	Singlet-A	6.5707 eV	188.69 nm	f=0.1430	<S**2>=0.000
	91 ->101	0.18572				
	91 ->102	0.19210				
	91 ->103	-0.14440				
	92 ->101	0.31872				
	96 ->102	0.26413				
	96 ->103	-0.12187				
	97 ->102	-0.14547				
	99 ->101	0.39506				

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