## SUPPORTING INFORMATION

	1	2	3	4
μ(D)	0.18	7.08	7.66	11.20
N-C1 (Å)	1.413	1.398	1.394	1.388
N-C5/N-C5' (Å)	1.411	1.417	1.418	1.420
C4-X (Å)	1.086	1.427	1.450	1.436

Table S1. DFT dipole moment  $\mu$  and characteristic bond lengths of compounds 1-4.

Table S2. Oxidation potentials  $(E^{\circ}_{ox})^{a}$ , ionization potentials (IP) measured by XPS, and gas phase TD-DFT energies of the HOMO-1, HOMO, LUMO, and LUMO+1 levels (PBE0 functional, 6-31G(d) basis) of compounds 1-4.

	1	2	3	4
$E^{\circ}_{1}$ vs Fc (V)	0.43	0.63	0.69	0.57
$E^{\circ}_{2}$ vs $Fc^{b}$ (V)	1.13	1.23	1.25	1.14
IP (XPS) (eV)	5.48	5.29	5.44	6.24
LUMO+1 (eV)	-0.46	-0.98	-1.03	-1.12
LUMO (eV)	-0.68	-1.17	-1.88	-2.37
HOMO (eV)	-5.03	-5.44	-5.55	-5.63
HOMO-1 (eV)	-6.18	-6.45	-6.48	-6.56

<sup>a</sup> dichloromethane solution containing 0.1 mol.L<sup>-1</sup> nBu<sub>4</sub>NPF<sub>6</sub> as an electrolyte,  $E_{ox}(Fc^+/Fc) = 0.52$  V versus ECS (0.251 V); <sup>b</sup> measured at 5 or 10 Vs<sup>-1</sup>.



Fig. S1. Energy evolution of the HOMO-1, HOMO, LUMO and LUMO+1 for compounds 1-4.



Fig. S2. DFT-computed frontier orbitals (HOMO-1, HOMO, LUMO and LUMO+1) in the gas phase for compounds 1-4

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**Fig. S3.** Transient absorption spectra of **1** in MeOH at different pump-probe time delays after excitation at 266 nm. The -1 ps trace corresponds to the spectral baseline in the absence of pump excitation. Reference steady-state absorption (dotted line) and fluorescence (full line) spectra of **1** in MeOH are also given (D). The spectral evolution can be interpreted with a three-step photophysical scheme (F).

The first step (0.5-0.8 ps range, part A) shows the growth of a TA band peaking at 485 nm and two negative components at 339 and 385 nm that correspond to GSB and SE bands, respectively ( $\tau_1 = 0.29 \pm 0.05$  ps). Although it is faster and less pronounced, this first dynamics looks like that one in the 0-2.5 ps range in HEX (Fig. 3) and can be similarly ascribed to the  $S_n \rightarrow S_1$  IC process.

A second step in the spectral evolution (2.5-50 ps range, part B), not observed in HEX, shows essentially a red-shift and a simultaneous decrease in intensity of the SE band. The peak position of the SE band moves from 385 nm at 1 ps, a value close to that found in HEX, to about 406 nm at  $t \ge 50$  ps, which corresponds to the position of the steady-state fluorescence ( $\lambda_{max} = 405$  nm, see part D). The GSB and TA bands remain nearly unchanged in this time domain. Obviously, this spectral change is due to the solvation of the S<sub>1</sub> state by the polar MeOH molecules. The time-dependent shift of the SE band peak position can be fit to a two-exponential kinetics (see part E). The longer time constant ( $\tau_2^{\text{shift}} = 15.6$  ps) matches well the slowest component of the solvent relaxation dynamics (15.3 ps<sup>1</sup>). The shorter time constant ( $\tau_1^{\text{shift}} = 1.2$  ps) is intermediate between the two main fast components of the solvent relaxation dynamics (0.28 and 3.20 ps, respectively<sup>1</sup>). The decrease in intensity of the negative SE band as it shifts to higher wavelengths is likely due to an increasing overlap with the positive broad TA band at 485 nm.

Finally, all transient signals decay in the 50-1500 ps (C) with a single-exponential kinetics ( $\tau_2 = 1.79 \pm 0.3$  ns), leading to some long-lived TA signal in the 500-700 nm region. This residual absorption can be related to the T<sub>1</sub> state spectrum characterized by nano-microsecond laser flash photolysis measurements (see Fig. S4).



**Fig. S4.** Laser flash photolysis spectra of the excited triplet state (T<sub>1</sub>) of **1** obtained at different time delays after excitation at 266 nm of a deoxygenated solution in (a) MeOH and (b) MeCN. The decay kinetics can be fit with a single-exponential function of time constant  $\tau_{T} = 4.2 \ \mu s$  and 3.8  $\mu s$  in MeOH end MeCN, respectively. As in HEX solution, drastic shortening of this decay is observed in the presence of dioxygen ( $\tau_{T} \le 50 \ ns$ ). This spectrum is similar to that found in HEX (Fig. 4). In the 180  $\mu s$  spectrum, some residual GSB signal remains after complete decay of the T<sub>1</sub> state features, together with weak TA bands in the 370-450 nm and 650-700 nm regions, and a broader TA band in the red part, peaking out of the experimental window. This residual spectrum, observed only in polar solvents, corresponds fairly well to the spectrum of the cation radical of **1**.<sup>2</sup> The broad red absorption might also have a contribution from the solvated electron<sup>3, 4</sup> which gives rise to a residual spectrum, superimposed to the T<sub>1</sub> spectrum at all delay times. These results indicate that, in polar solvents, **1** undergoes minor photoionization by one photon absorption, as frequently observed for aromatic amines having a low ionization potential.<sup>5</sup>



**Fig. S5**. Transient absorption spectra of **2** in HEX at different pump-probe time delays after excitation at 266 nm (A-C) and the corresponding photophysical scheme (D). The -1 ps trace corresponds to the spectral baseline in the absence of pump excitation. Reference steady-state absorption (dotted line) and fluorescence (full line) spectra of **2** in HEX are also given (C). A first step of the spectral evolution (0.5-1.0 ps range, part A) shows the growth of a TA band at 480 nm and of a negative GSB band at 330 nm ( $\tau_1 = 0.37 \pm 0.05$  ps). The spectral dip noticed at 395 nm at the position of the fluorescence maximum is ascribed to the negative SE component overlapped with the broad TA band. This evolution is similar to that of compound **1** in HEX in the 0-2.5 ps range (Fig. 3) and ascribed by analogy to the  $S_n \rightarrow S_1(\pi\pi^*)$  IC process. It is followed in the 50-1500 ps range (part B) by the single-exponential decay of the 480 nm TA band concomitantly with the growth of a new TA band peaking at 585 nm with a common time constant of  $\tau_2 = 1.81 \pm 0.40$  ns). This evolution is characterized by four isosbestic points at 388, 403, 540, and 673 nm. The dashed line in part B represents the spectrum of the triplet excited state T<sub>1</sub> obtained after subtracting the 50 ps spectrum from the 1500 ps one, after normalization. This spectrum is similar to the T<sub>1</sub> state spectrum identified from nano-microsecond laser flash photolysis measurements (see Fig. S6).



**Fig. S6.** Laser flash photolysis spectra of the excited triplet state (T<sub>1</sub>) of **2** obtained at different time delays from 0.5 to 40 µs after excitation at 266 nm of a deoxygenated solution in HEX. The decay kinetics can be fit with a single-exponential function of time constant  $\tau_{\rm T} = 6.7$  µs (inset: 590 nm kinetics), drastically shortened in the presence of air ( $\tau_{\rm T} \le 50$  ns). The complete disappearance of all transient signals (GSB and TA) at the end of the decay kinetics, as for compound **1**, signs the full recovery of the ground state population from T<sub>1</sub> and the absence of any noticeable photoproduct.



**Fig. S7**. Transient absorption spectra of **2** in HEX at different pump-probe time delays after excitation at 383 nm (only the region 400-700 nm is probed). The shortest time spectrum is similar to that observed at delay times longer than 1 ps in the spectra recorded upon 266 nm pump excitation (Fig. S5), assigned to the excited  $S_1$  state. The ultrafast  $S_n \rightarrow S_1$  IC process arising when exciting at 266 nm is not observed, as expected from the absence of  $S_n$  population upon pumping at 383 nm. A first step of the spectral evolution (0.5-20.0 ps range, part B) shows a narrowing of the TA band on its red side, typical of vibrational cooling. It is followed (20-900 ps range, part B) by the decay of the  $S_1$  state spectrum and concomitant rise of the  $T_1$  state spectrum, similarly as with 266 nm excitation.



**Fig. S8.** Transient absorption spectra of **2** in MeCN at different time delays after excitation at 266 nm. For clarity, the spectral evolution is separated in 2 time domains 0-50 ps (A) and 50-1500 ps (B). The pump-probe time delays are given. The -1 ps trace corresponds to the spectral baseline in the absence of pump excitation. Reference steady-state absorption (dotted line) and fluorescence (full line) spectra of **2** in MeCN are also given (C).

In the 0-50 ps time domain (part A), a spectrum similar to that observed for the emissive  $S_1$  state in HEX rises (TA band at 468 nm and GSB band at 336 nm,  $\tau_1 = 0.45 \pm 0.1$  ps) and evolves almost simultaneously toward a new spectrum (TA band at 420 nm and SE component at 513 nm roughly matching the fluorescence spectrum,  $\tau_2 = 0.80 \pm 0.1$  ps). By analogy with the spectral evolution in MeOH, the  $\tau_1$  and  $\tau_2$  dynamics can be ascribed to the  $S_n \rightarrow S_1$  IC and  $S_1 \rightarrow S_1$ ' processes, respectively, where  $S_1$ ' is the emissive excited state stabilized in MeCN. Note that the  $S_1$ ' rising kinetics also includes a minor component ( $\tau_2$ ' = 47 ± 2 ps, 5%) that remains not clearly understood. Then, at times longer than 50 ps (part B), the  $S_1$ ' spectrum decays with single-exponential kinetics ( $\tau_3 = 4.0 \pm 0.7$  ns) approximately matching the fluorescence lifetime ( $\tau_F = 4.58$  ns).



**Fig. S9.** Laser flash photolysis spectra of the excited triplet state (T<sub>1</sub>) of **2** obtained at different time delays from 1.5 to 45  $\mu$ s after excitation at 266 nm of a deoxygenated solution in MeCN. The decay kinetics can be fit with a single-exponential function of time constant  $\tau_{\rm T} = 7.3 \,\mu$ s, drastically shortened in the presence of dioxygen ( $\tau_{\rm T} \le 50 \,$ ns). As for compound **1**, the subsistence of an extremely weak residual spectrum after complete decay of the T<sub>1</sub> bands (see the 45  $\mu$ s trace), not observed in the nonpolar solvent HEX, is assigned to the formation of a radical cation via photoionization.



**Fig. S10**. Transient absorption spectra of **3** in HEX at different pump-probe time delays after excitation at 266 nm. For clarity, the spectral evolution is separated in 2 time domains 0-17 ps (A) and 200-1000 ps (B). The pump-probe time delays are given. The -1 ps trace corresponds to the spectral baseline in the absence of pump excitation. Reference steady-state absorption (dotted line) and fluorescence (full line) spectra of **3** in HEX are also given (C).



**Fig. S11**. (A) Laser flash photolysis spectra of the excited triplet state (T<sub>1</sub>) of **3** obtained at different time delays from 0.5 to 28 µs after excitation at 266 nm of a deoxygenated solution in HEX and (B) reference steady-state absorption spectrum of **3** in HEX (dotted line). The decay kinetics monitored at 700 nm (inset) can be fit with a single-exponential function of time constant  $\tau_{T} = 9.1$  µs, drastically shortened in the presence of dioxygen ( $\tau_{T} \le 100$  ns).



**Fig. S12.** Kinetic plots measured from transient absorption for **3** in MeCN at 370 nm (A), 445 nm (B), 462 nm (C), and 585 nm (D) and best multiexponential fit. The corresponding time constants are displayed (d = decay, g = growth). Note that a growing component is necessary to get a correct fit of the 445 and 462 nm kinetics in the 2-15 ps time range. As discussed in the text, this component accounts for the appearance of the hot ground state TA signal at 460 nm (red-shifted from the steady-state S<sub>0</sub> absorption) from depopulation of the excited state.



**Fig. S13**. (A) Laser flash photolysis spectra of the excited triplet state (T<sub>1</sub>) of **3** obtained at different time delays from 0.4 to 48 µs after excitation at 266 nm of a deoxygenated solution in MeCN and (B) reference steady-state absorption spectrum of **3** in MeCN (dotted line). The decay kinetics monitored at 700 nm (inset) can be fit with a single-exponential function of time constant  $\tau_T = 7.3$  µs, drastically shortened in the presence of dioxygen ( $\tau_T \le 100$  ns).



**Fig. S14**. Transient absorption spectra of **3** in BuCN at different pump-probe time delays after excitation at 400 nm. For clarity, the spectral evolution is separated in 4 time domains 0-0.7 ps (A), 0.7-4.0 ps (B), 4-17 ps (C), and 14-70 ps (D). The pump-probe time delays are given. The area around 400 nm is wiped out due to the pump-pulse related noise. The spectral evolution is similar to that in MeCN and BuCN and can be interpreted on the basis of the same reaction scheme:  $ICT^{(FC)} \rightarrow ICT$  ( $\tau_1 = 0.17$  ps)

ICT  $\rightarrow$  ICT  $(\tau_1 = 0.17)$  ICT ICT  $\rightarrow$  ICT  $(\tau_2 = 1.1 \text{ ps})$ ICT  $\rightarrow S_0^{\text{hot}} (\tau_3 = 8.5 \text{ ps})$ 

 $S_0^{\text{hot}} \rightarrow S_0 \quad (\tau_3 - 8.5 \text{ p})$  $S_0^{\text{hot}} \rightarrow S_0 (\tau_4 \sim 6.0 \text{ ps})$ 

In the 14-70 spectral evolution (part D), the decay of the GSB signal at 380 nm and of the TA signal at 450 nm are slightly retarded relative to the decay of the TA band at 600 nm, which arises from the presence of the  $S_0^{hot}$  cooling dynamics (time  $\tau_4$ ), as in MeCN, subsequently to the ICT" depopulation process (time  $\tau_3$ ). However, whereas in MeCN these two processes were well distinguishable spectrally as  $\tau_3 \ll \tau_4$ , in BuCN they are much less differentiated in time and the cooling dynamics is hard to detect.



**Fig. S15**. Transient absorption spectra of **3** in OcCN at different pump-probe time delays after excitation at 400 nm. For clarity, the spectral evolution is separated in 4 time domains 0-0.7 ps (A), 0.6-14 ps (B), 14-40 ps (C), and 50-230 ps (D). The pump-probe time delays are given. The area around 400 nm is wiped out due to the pump-pulse related noise. The spectral evolution is similar to that in MeCN and BuCN and can be interpreted on the basis of the same reaction scheme:  $ICT^{(FC)} \rightarrow ICT$  ( $\tau_1 = 0.15 \text{ ps}$ )  $ICT \rightarrow ICT$ " ( $\tau_2 = 5.5 \text{ ps}$ )

ICT"  $\rightarrow$  S<sub>0</sub> ( $\tau_3 = 35$  ps)

In this case, the depopulation of the ICT" state ( $\tau_3 = 35$  ps) is much slower than the subsequent S<sub>0</sub> cooling process which becomes imperceptible. The GSB decay and ICT" TA band decay have same kinetics. Thus, after complete depopulation of the ICT state (t > 20 ps), all spectra consist essentially of the ICT" TA spectrum truncated by the GSB bands at 320 and 380 nm.



**Fig. S16**. Transient absorption spectra of **3** in THF at different pump-probe time delays after excitation at 400 nm. For clarity, the spectral evolution is separated in 3 time domains 0-0.8 ps (A), 0.7-9 ps (B), and 9-300 ps (C). The pump-probe time delays are given. The area around 400 nm is wiped out due to the pump-pulse related noise. The spectral evolution is similar to that in MeCN and BuCN and can be interpreted on the basis of the same reaction scheme:

 $ICT^{(FC)} \rightarrow ICT \ (\tau_1 = 0.2 \text{ ps})$ 

ICT  $\rightarrow$  ICT" ( $\tau_2 = 1.2 \text{ ps}$ )

ICT"  $\rightarrow$  S<sub>0</sub> ( $\tau_3 = 150 \text{ ps}$ )

As in OcCN, the depopulation of the ICT" state ( $\tau_3 = 150 \text{ ps}$ ) is much slower than the subsequent S<sub>0</sub> cooling process, which is not detectable.



Fig. S17. Spectral shift (nm) as a function of time of the SE band maximum  $\lambda^{max}(t)$  of 3 in various solvents, with  $\lambda^{max}(t_0)$  featuring the initial position.



**Fig. S18**. Transient absorption spectra of **4** in MeCN at different pump-probe time delays after excitation at 390 nm (from ref. 6). For clarity, the spectral evolution is separated in 4 time domains 0-1.4 ps (A), 1-4 ps (B), 3.4-12 ps (C), and 12-60 ps (D). The pump-probe time delays are given. Reference steady-state absorption (dotted line) and fluorescence (full line) spectra of **4** in MeCN are also shown (E).



**Fig. S19**. Transient absorption spectra of **4** in EtOH at different pump-probe time delays after excitation at 390 nm (from ref. 6). For clarity, the spectral evolution is separated in 4 time domains 0-2.7 ps (A), 3.4-12 ps (B), 17-75 ps (C), and 75-200 ps (D). The pump-probe time delays are given.



**Fig. S20**. (A) Laser flash photolysis spectra of the excited triplet state (T<sub>1</sub>) of **4** obtained at different time delays from 0.22 to 4 µs after excitation at 266 nm of a deoxygenated solution in TOL and (B) reference steady-state absorption spectrum of **4** in TOL (dotted line). The decay kinetics monitored at 650 nm (inset) can be fit with a single-exponential function of time constant  $\tau_T = 0.8$  µs, drastically shortened in the presence of dioxygen ( $\tau_T \le 100$  ns).

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