

Electronic Supplementary Information (ESI) for

Electronic structure calculations and physicochemical experiments quantify the competitive liquid ion association and probe stabilisation effects for nitrobenzospiropyran in phosphonium-based ionic liquids

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ESI 1 - Detailed anion:MC electronic structures calculated with the MP2 method: This section provides a comparison of B3LYP and MP2 calculated anion-MC complexes. While the post-Hartree Fock MP2 method provides stronger dispersion forces than the HF-DFT hybrid B3LYP functional and so larger magnitude ΔE values (Table S1), the general features of the probe-ion complex geometries are preserved (Figures S1-S3) and the anion-dependent complexation energy difference $\Delta\Delta E$ is similar for both methods, -0.18 eV for MP2 (Table S1) compared with -0.25 eV for B3LYP.

Table S1. Anion-probe complex properties calculated with the MP2 wavefunction.

Complex	Close contact distances (Å)	ΔE (eV)	Δq (a.u)
$Cl^- : MC$	3.1 ($Cl : H_{N-CH3}$); 2.6 ($Cl : H_{CH3}$) 3.1 ($Cl : N$)	-1.38	-0.03
$NTf_2^- : MC$	2.3 ($O_{-S} : H_{CH3}$); 2.8 ($O_{-S} : H_{C6H6}$) 2.7 ($N : H_{N-CH3}$); 3.1 ($N_{NTf2} : N_{MC}$)	-1.21	-0.02

Geometries and electronic structures calculated with MP2/6-311++G** model chemistry, as described in the main text. ΔE is the binding energy of the complex, as computed from the MP2 energy of the complex relative to the MP2 energies of the isolated species.

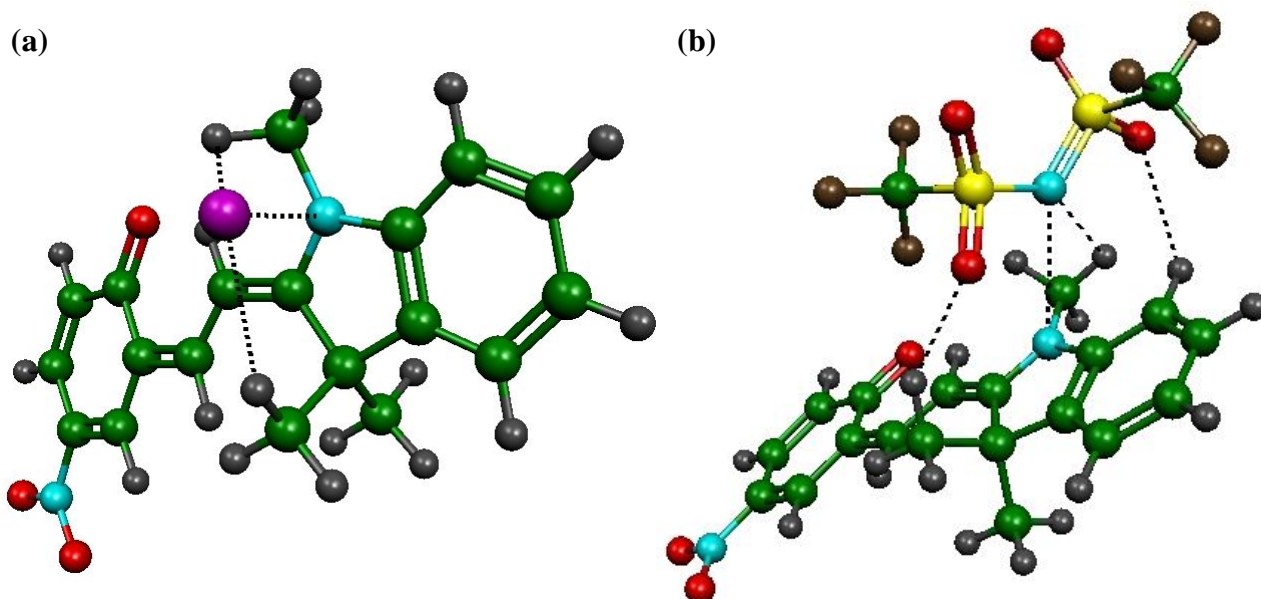


Figure S1. Complexation geometries with close contacts (given in Table S1) marked by dashed lines for charged ion-probe complexes, panel (a) the anionic complex with Cl⁻ and (b) the anionic complex with NTf₂⁻; carbon atoms are green, hydrogens are grey, chlorines are magenta, nitrogens are cyan, oxygens are red, sulphurs are yellow and fluorine atoms are brown.

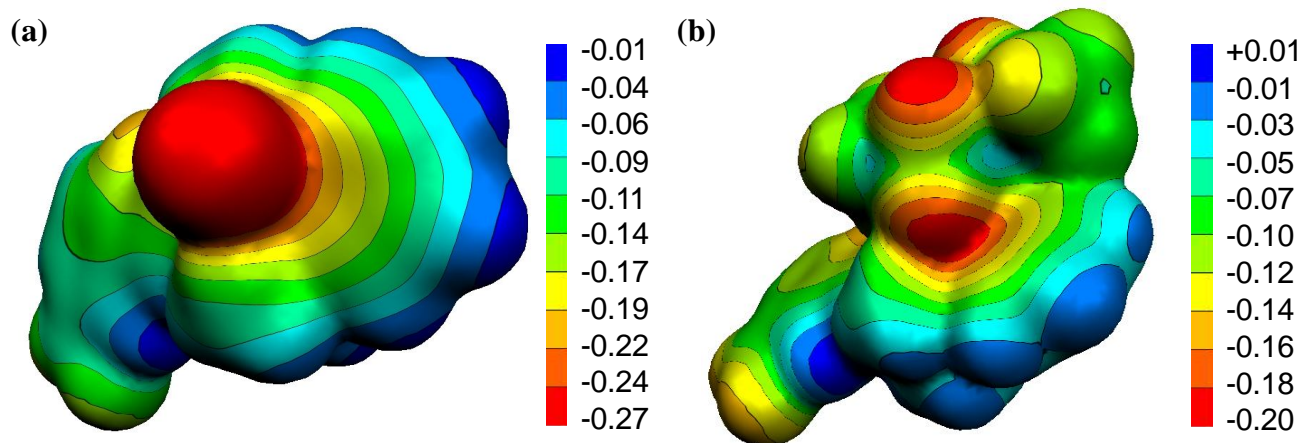


Figure S2. Computed Molecular Electrostatic Potential (MEP) surfaces generated as described in the main text and with surfaces coloured according to regions of net charge as marked in the scale bars, with the scale set in each case according to the largest net negative and net positive sites in each charged ion-probe complexes, panel (a) the anionic complex with Cl⁻ and (b) the anionic complex with NTf₂⁻.

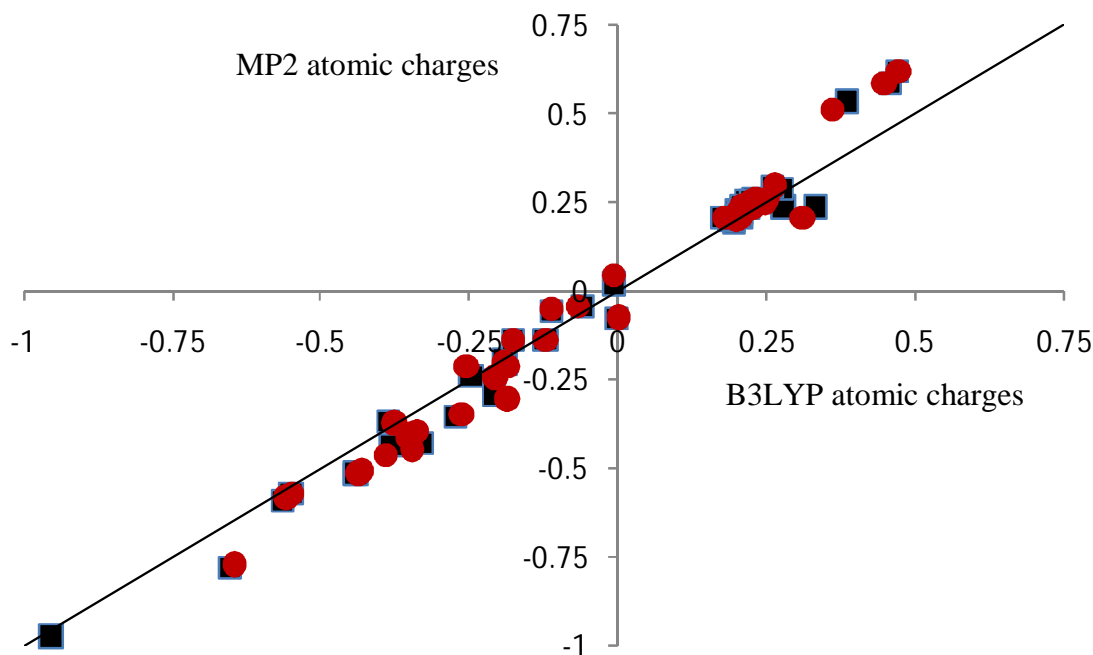


Figure S3. Plots of MP2 vs. B3LYP natural population (see main text) atomic charges computed for **(blue squares)** the anionic **MC:Cl** complex and **(red circles)** the anionic **MC:NTf₂⁻** complex. The $y=x$ black line is included to guide the eye; the magnitudes of the atomic charges are generally slightly larger in the MP2 calculations and both datasets would fit $y=1.1x$ lines (not shown) with $R^2 > 0.95$.

ESI 2 - Computed [emIm][NTf₂] and emIm⁺:MC complexes: Panel (a) of Figure S4 shows the computed geometries and electrostatic potential surfaces for the emIm⁺ cation paired with the NTf₂⁻ anion. The emIm⁺ complex with Cl⁻ is given in Figure 2 of the main text. Panel (b) of Figure S4 shows the computed geometries and electrostatic potential surfaces for the emIm⁺ cation coordinating the **MC** probe. The corresponding 3-site complexes describing probe stabilisation by the emIm-based ILs are given Figure 4 of the main text. Figure S5 gives the near-Fermi MO diagram for [emIm][NTf₂] together with the MO surfaces that serve to explain some of the observed features in the experimental valence band spectrum (references 21 and 53 in the main

text). The MO diagram shows a moderate HOMO-LUMO gap of -6 eV between the LUMO (a cation ring anti-bonding orbital), and the HOMO (dominated by the anion and principally centered on nitrogen), together with near-lying occupied orbitals composed of both anion- and cation-centered orbitals.

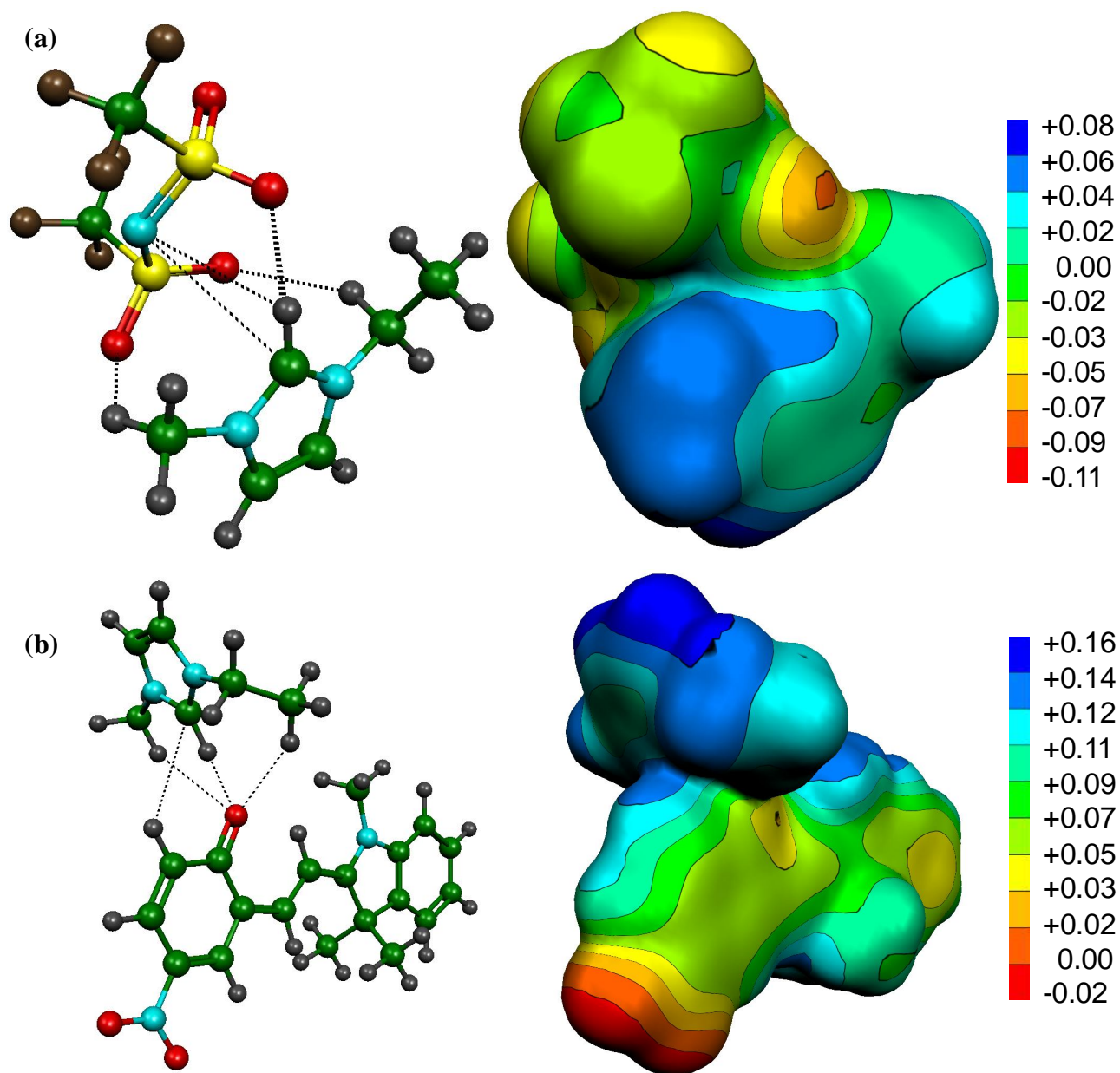


Figure S4. Complexation geometries with close contacts (the corresponding distances are given in Table 1 of the main text) marked by dashed lines for (a) net neutral [emIm][NTf₂] and (b) the cationic emIm⁺·MC complex; carbon atoms are green, hydrogens grey, chlorines magenta, nitrogens cyan, oxygens red, sulphurs yellow and fluorine atoms are brown. Also shown are

computed Molecular Electrostatic Potential (MEP) surfaces generated as described in the text and with surfaces coloured according to regions of net charge as marked in the scale bars, with the scale set in each case according to the largest net negative and net positive sites in each complex.

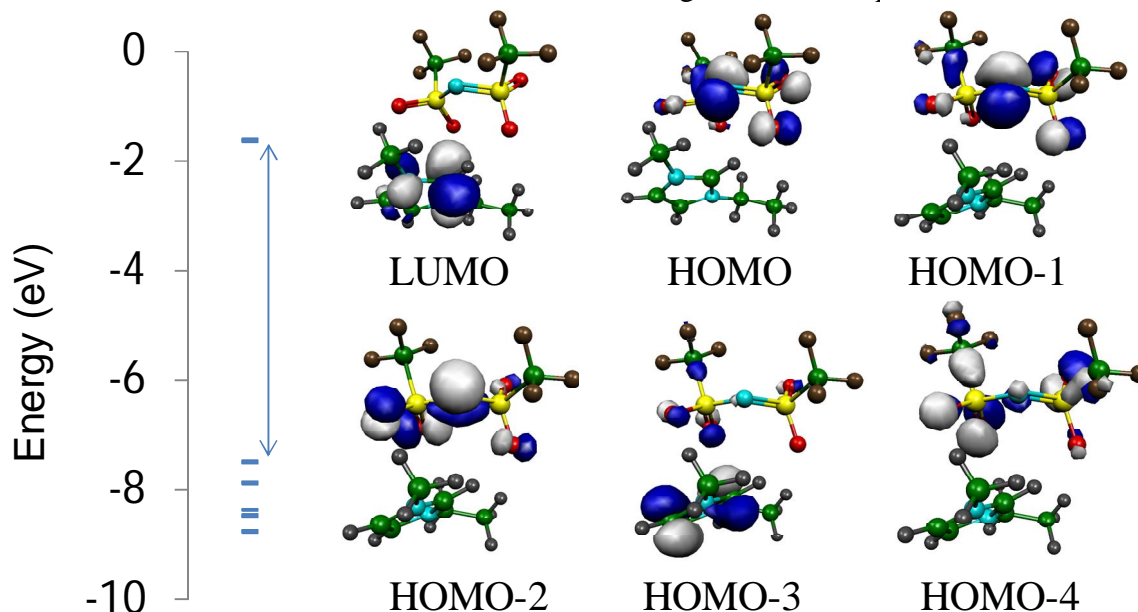


Figure S5. MO diagram with HOMO-LUMO gap as marked, and selected MO surfaces shown (LUMO, HOMO, HOMO-1, HOMO-2, HOMO-3 and HOMO-4) for the net neutral [emIm][NTf₂] complex; carbon atoms are green, hydrogens grey, chlorines magenta, nitrogens cyan, oxygens red, sulphurs yellow and fluorine atoms are brown.

ESI 3 - Control IL:probe simulations replacing MC with the closed SP isomer: The solvent-perturbed probe photochromism described in this work relies on the stronger interaction of the IL medium with the zwitterionic **BSP** isomer **MC**. Reported below are computed complexes for Cl⁻, NTf₂⁻ and emIm⁺ with the closed **SP** isomer, together with the corresponding 3-site complexes featuring both IL ions complexed to **SP**. Table S2 and Figure S6 show the interactions with the closed state; as shown in Figure 1 in the main text, the closed **SP** isomer features regions of net negative charge centered on the “elbow” between the indoline ring nitrogen and pyran ring nitrogen (maximum negative electrostatic potential is -0.08 a.u., lower than the -1.00 a.u. for the open **MC** form) and net positive charge centered on the phenyl hydrogens on the nitrobenzene

moeity (maximum positive electrostatic potential is +0.05 a.u., lower than the +0.07 a.u. for the open **MC** form). These weaker interactions for the closed state are reflected in the lower complexation energies given in Table S2, the individual ion interactions with **SP** are only approximately ¼ (cation interactions with the sterically-constrained N--O “elbow”) and ½ (anion interactions with the phenyl hydrogens of the nitrobenzene group) that of the corresponding **MC**:ion binding strengths given in Table 1 in the main text. The net complexation energy available for the full IL:probe complexes, subtracting the intra-IL association energy from the IL:probe complexation energy, is at best approximately ⅓ that available with the **MC** zwitterion, illustrating that the primary effect of the IL medium will be in prolonging the lifetime of the zwitterion with a smaller effect on the stability of the closed form. In essence the calculations support the chemical intuition that the IL will have a much larger influence on the stability of the open rather than closed isomer of the **MC**↔**SP** photoswitch.

Table S2. Calculated **SP**:ion and **SP**:IL complex properties.

Complex	Close contact distances (Å)	ΔE (eV)	%ΔE vs. MC
Cl ⁻ : SP	2.3 (<i>H_{Ph}:Cl</i>)	-0.56	57
NTf ₂ ⁻ : SP	2.3 (<i>O:H_{CH3N}</i>); 2.5 (<i>O:H_{CH3C}</i>); 2.5 (<i>O:H_{Ph}</i>)	-0.37	51
emIm ⁺ : SP	2.4 (<i>H_{CH3}:N</i>); 2.5 (<i>H_{CN2}:O</i>)	-0.20	26
emIm ⁺ : SP : Cl ⁻	3.0 (<i>H_{CH3}:Cl</i>); 2.7 (<i>C_{CN2}:Cl</i>); 2.6 (<i>H_{CN2}:Cl</i>); 2.9 (<i>H_{CH2}:Cl</i>); 2.6 (<i>H_{Ph}:Cl</i>)	-0.20	32
emIm ⁺ : SP : NTf ₂ ⁻	3.2 (<i>C_{CN2}:O</i>); 2.4 (<i>H_{CH3}:O</i>); 2.0 (<i>H_{CN2}:N</i>); 2.7 (<i>H_{CN2}:O</i>); 2.9 (<i>H_{CN2}:O</i>); 2.3 (<i>H_{CH2}:O</i>); 2.6 (<i>H_{Ph}:O</i>); 2.5 (<i>H_{CH3C}:O</i>); 2.5 (<i>H_{CH3N}:O</i>)	-0.19	30

Geometries and electronic structures calculated with B3LYP/6-311++G**, as described in the main text. ΔE calculated as for the **MC** complexes, comparing two-species complexes with isolated species and full IL:probe three-species complexes with isolated probe and both IL ions. %ΔE values compare complexation energies with closed **SP** to those calculated for open **MC** (Table 1 in the main text).

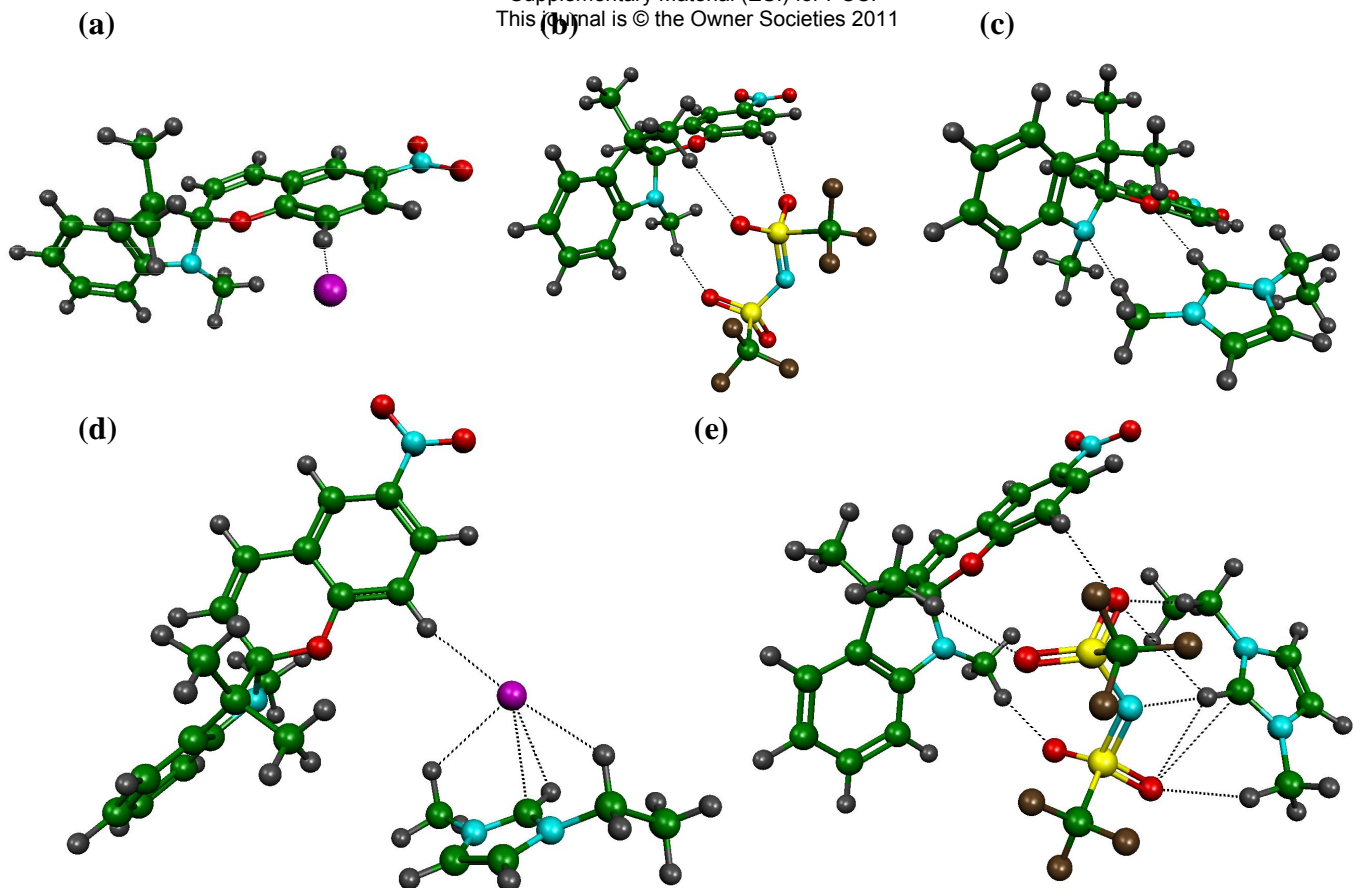


Figure S5. Complexation geometries with close contacts marked by dashed lines and distances given in Table S2 for (a) the anionic $\text{Cl}^-:\text{SP}$ complex, (b) the anionic $\text{NTf}_2^-:\text{SP}$ complex, (c) the cationic $\text{emIm}^+:\text{SP}$ complex, (d) the net neutral $\text{emIm}^+:\text{SP}:\text{Cl}^-$ complex and (e) the net neutral $\text{emIm}^+:\text{SP}:\text{NTf}_2^-$ complex; carbon atoms are green, hydrogens are grey, chlorines are magenta, nitrogens are cyan, oxygens are red, sulphurs are yellow and fluorine atoms are brown.