Supporting information for:

## Diasereoselective supramolecular ion-pairing between TRISPHAT anion and *pro*-chiral heptamethine cyanine dye.

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## X-ray crystallography.

*Data collection:* For compounds [1][*rac*-TRISPHAT], processing of the data was performed by the KappaCCD analysis softwares.<sup>1</sup> The lattice constants were refined by least-square refinement using 7191 reflections  $(1.07^{\circ} < \theta < 27.8^{\circ})$ .

Structure solution and refinement: [1][rac-TRISPHAT] crystallize in the triclinic system and according to the observed systematic extinctions, the structures have been solved in the *P-1* space group (No. 2). The structure was solved by direct methods using the SIR97 program<sup>2</sup> combined to Fourier difference syntheses and refined against *F* using reflections with  $[I/\sigma(I) > 2]$  with the CRYSTALS program<sup>3</sup>. All atomic displacements parameters for non-hydrogen atoms have been refined with anisotropic terms. After anisotropic refinement, all the hydrogen atoms are found with a Fourier Difference. Table 1 summarizes the crystallographic data and refinement details for [1][*rac*-TRISPHAT].

	[1][rac-TRISPHAT]
Formula	$C_{66}H_{52}Cl_{13}N_2O_6P$
$f.w. (g.mol^{-1})$	1461.01
Cryst. Syst.	Triclinic
Space group	<i>P-1</i> (No. 2)
a (Å)	13.673 (5)
b (Å)	14.213 (5)
c (Å)	20.031 (5)
α (°)	73.329 (2)
β (°)	89.059 (5)
γ (°)	62.217 (3)
V (Å <sup>3</sup> )	3267.5 (2)
Z	2
T (K)	293
λ(ΜοΚα) (Å)	0.71069
$D(g.cm^{-3})$	1.485
$\mu$ (mm <sup>-1</sup> )	0.63
$R(F)^{a}$ , I>1 $\sigma$ (Fo)	0.051
$R_w(F^2)^b$ , I>1 $\sigma(Fo)$	0.050
S	1.10
Rint	0.048
θmax	27.8°
h	<b>-</b> 17 → 17
k	$-18 \rightarrow 18$
1	$-26 \rightarrow 26$
Parameters	793
Measured reflections	27915
Independent reflections	15362
Reflections with I >	7191
$\Delta \rho_{min}$	-0.33 e Å <sup>-1</sup>
$\Delta \rho_{max}$	0.61 e Å <sup>-1</sup>
$a \mathbf{P}(\mathbf{E}) = \sum   \mathbf{E}_{\mathbf{C}}    \mathbf{E}_{\mathbf{C}}     \mathbf{\Sigma}  \mathbf{E}_{\mathbf{C}}  ^{\mathbf{b}} \mathbf{P}$	$(E) = \sum [w ((Eo^2 Eo^2)^2 / \sum w Eo^4]^{1/2}$

 Table 1: Crystal data and structure refinement parameters.

 $^{a}R(F) = \Sigma ||Fo| - |Fc|| / \Sigma ||Fo|, ^{b}R_{w}(F) = \Sigma [w ((Fo^{2} - Fc^{2})^{2} / \Sigma wFo^{4}]$ 

*Crystal packing description.* Chromophore  $1^+$  crystallize in a triclinic and centrosymmetric space group. The crystal lattice in  $\mathbf{1}^+$  is constituted of layers of molecules linked together by C-H··· $\pi$  (d  $\approx$  3.1 Å) bonds between axials hydrogen from the central 6-members ring and to an

aromatic cycle of the Trisphat counter-anion. One benzyl group interacts with Trisphat, hence that ensure the crystal cohesion by  $\pi$ -stacking.



Figure S1 : aromatic region of the <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, RT, 50.32 MHz) of [1][Br] (up) and [1][( $\Delta$ -TRISPHAT] (down). (NMR signal of C<sub>1</sub> appears in the grey area)



Figure S2. Aromatic region of <sup>1</sup>H NMR (RT, 500 MHz) of [1][ $\Delta$ -TRISPHAT] in DMSO- $d_6$  (a),

 $\text{CDCl}_3$  (b), benzene- $d_6$  (c)



Figure S3: Aromatic region of <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>, RT, 500 MHz) of [1][Δ-TRISPHAT] (up), [1][*rac*-TRISPHAT] (middle), [1][Λ-TRISPHAT] (down)

<sup>1</sup> Nonius, *Kappa CCD Program Package: COLLECT, DENZO, SCALEPACK, SORTAV*, Nonius B. V., Delft, The Netherlands, 1999.

<sup>2</sup> G. Cascarano, A. Altomare, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, D. Siliqi, M.
C. Burla, G. Polidori, M. Camalli, *Acta Crystallogr.*, 1996, A52, C-79.

<sup>&</sup>lt;sup>3</sup> D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge, *CRISTAL Issue 11*, CRISTAL Issue 11, Chemical Crystallography Laboratory, Oxford, UK, 1999.