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

Pierre-Antoine Bouit, Christophe Aronica, Laure Guy, Alexandre Martinez, Chantal Andraud, Olivier Maury*

The supramolecular interactions between enantiopure TRISPHAT anion (tris(tetrachlorobenzenediolato)phosphate) and various non chiral or *pro*-chiral heptamethine cyanine cations have been studied in the solid state by X-rays diffraction and in solution by NMR spectroscopy. The presence of the conformationnally restricted *ter*-butyl functionnalized cyclohexenyl moieties is responsible for the asymmetric shape interaction between the two ions revealing the chirality of the molecule. On the other hand, the strength of this interaction is controlled by the nature of the distal substituents.

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Introduction

Since its discovery in 1997 by Lacour and co-workers[1] and its large scale resolution,[2] enantiopure TRISPHAT anion (tris(tetrachlorobenzenediolato)phosphate, Figure 1) has been extensively used to induce supramolecular ion-pairing associations with chiral organic, organometallic or coordination cationic compounds.[3] This D_3-symmetric anion presents a wide range of extremely interesting properties and for example can act as an efficient NMR chiral shift-reagents for enantiodifferentiation of cations,[4] as a chiral inducer onto labile cation[5] and as chiral auxiliary for ion-pair mediated resolution properties by preferential extraction or chromatography.[3,6] Owning to these very special properties and to the quite easy synthesis and resolution, TRISPHAT anion is now largely disseminate in the scientific community and is becoming a classical resolution auxiliary for many groups around the world.[7] During the course of our researches aiming at the design of chromophores for nonlinear optical (NLO) applications, we fortunately discovered that, the strong lipophilic character of TRISPHAT anion, already known to deeply modify the chromatographic properties of the associated cation, is also able to greatly enhance its solubility in organic solvents. This particularity is very convenient for the synthesis and purification of polymers or dendrimers,[8] and is a real advantage for the experimental determination of the nonlinear efficiency for which high concentrations are needed. This high solubility requirement is particularly crucial for solution nonlinear transmittance measurements, a third order nonlinear process for which chromophores concentration about 100-300 g L^{-1} are commonly used. Such measurements are the key step for the design of optical limiters that are devices able to protect optical sensors like eyes or camera against damages caused by high-energy laser illumination but remaining transparent as long as the light intensity stands below the sensor safety threshold.[9] In this context, we recently reported the optical limiting behavior of cyanine dyes in the near infra-red around telecommunication wavelength (1,5 µm).[10] In order to improve the global efficiency of this system, we sought to further increase the solubility of the cationic heptamethine dyes by association with the TRISPHAT anion. In this article, we describe the unexpected formation of a diastereoselective ion-pairing between heptamethine cyanine and enantiopure TRISPHAT occurring in solid state as well in solution on the basis of X-rays diffraction analysis and NMR spectroscopy.

Results and discussion.

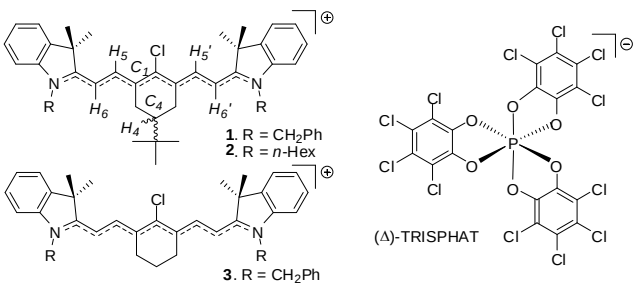

Fig 1. Structure of the studied molecules

Synthesis. The cyanine dyes studied in this article (Figure 1) differs by the functionalisation (or not) of the central cyclohexenyl ring by ^{t}Bu fragment [**1**][Br], (resp [**3**][Br]) and by the distal benzyl or n-hexyl moieties ([**1**][Br] and [**2**][I] respectively). All these compounds were prepared according to the literature.[10,11] In all cases, as expected the cationic

charge is fully delocalized between the two amino donor groups linked by a seven sp^2 hybridized carbon atoms squeleton. The planarity of the π-conjugated backbone is ensured by the locked six-member ring and due to the odd number of carbon atoms in the π-system, all C-C bonds are equivalents, intermediate between simple and double bonds.[10,11] As a result, the three molecules present a symmetry plane containing the Cl, C_1, C_4 and H_4 atoms (Figure 1) and therefore their ^{1}H NMR spectra (Figure 3a in the case [**1**][Br]) present a single set of signals for the two vinylic protons (H_5/$H_{5'}$ and H_6/$H_{6'}$, Figure 1). It is worth noting that owning to the presence of a symmetry plane, these dyes are not chiral, but the C_4 atom in compounds $\mathbf{1}^+$, $\mathbf{2}^+$ featuring a ^{t}Bu fragment bears two *pro*-chiral substituents. Consequently, any breaking of the planar symmetry will lead to the formation of two enantiomers.[12]

Associations of cyanine dyes [**1-3**][X] (X = Br, I) with 90% ee [cyn][*Δ*-TRISPHAT] (cyn = cynchonidinium)[1,2] were carried out by mixing equivalent amounts of both salts in dichloromethane solution at room temperature. The desired [**1-3**][*Δ*-TRISPHAT] were purified by chromatography (SiO_2, eluent CH_2Cl_2) as the most eluted compounds. As already observed, replacement of counter-anion by TRISPHAT results in a deep modification of the chromatographic behavior. For instance, in the case of $\mathbf{1}^+$, the bromide salt was eluted with a CH_2Cl_2–methanol 9/1 mixture. Such modification of chromatographic conditions is classical and can be ascribed to the stronger lipophilic character of TRISPHAT anion.[3,13] Compounds [**1-3**][*Δ*-TRISPHAT] were characterized by ^{1}H and ^{13}C NMR and gave satisfactorily elemental analysis (see experimental).

Solid state structure. Attempts to crystallize [**1**][*Δ*-TRISPHAT] (90% ee) by slow evaporation of methanol-toluene solution resulted in the formation of single crystal belonging to the centrosymmetric P-1 space group (N°2) of the racemate [**1**][*rac*-TRISPHAT] containing equal amount of [**1**][*Δ*-TRISPHAT] and [**1**][*Λ*-TRISPHAT]. Crystal data, refinements parameters and details of the crystallographic packing are reported in the ESI. On the molecular scale (Figure 2), the cation $\mathbf{1}^+$ presents a *syn*-type arrangement with the two N atoms on the same side of the methine chain as already observed for other cyanines and a remarkable planarity without any significant twist of the nine C(sp^2) carbon skeleton (overall tilt angles is 26°).[14] As expected for cyanine-like compounds, the conjugated backbone shows a "polyacetylene-type" stucture with equal C-C bond lengths (139 ± 2 pm) intermediate between single and double bonds (see table in ESI). This result indicates that the charge is perfectly delocalized between the two distal heterocycles. The planarity is enforced by the fused central cyclohexenyl ring that presents a chair conformation constrained by the thermodynamically favoured equatorial position of the ^{t}Bu fragment.[10,14c] This rigid conformation defines two diastereotopic faces according to the position of the out-of-plane C_4 atom with respect to the π-conjugated system (gray plan, Figure 2): The face II contains the C_4 carbon and therefore the bulky ^{t}Bu fragment whereas the opposite face I

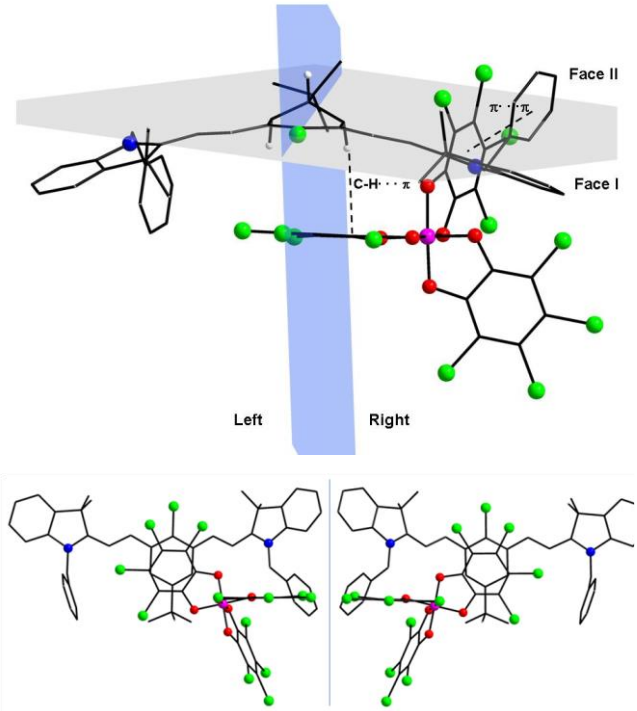

Fig 2: X-ray structure of [**1**][*rac*-TRISPHAT], H atoms were omitted for clarity except those involved in supramolecular interactions. (up) representation of the two non-equivalents faces of cyanine cation and supramolecular interaction between $\mathbf{1}^+$ and *Δ*-TRISPHAT; (bottom) representation of the two component of the crystal of [**1**][*Δ*-TRISPHAT] (right) and [**1**][*Λ*-TRISPHAT] (left).

is less sterically hindered. It is woth noting that the bulky TRISPHAT anion is located on this less sterically hindered face I (Figure 2). Furthermore, on this latter face, the presence of the two distal functionalisations on the amino donor groups define two cavities (noted right and left) on both sides of the symmetry plane (blue plane, Figure 2), mirror image one from each other. It is important to remark that *Δ*-TRISPHAT (resp, *Λ*-TRISPHAT) anion interacts selectively with the right (resp, left) side cavity. This selective recognition according to the lock-and-key principle is due to the TRISPHAT helicity. The cohesion of this association is ensured by (i) one C-H···π interaction (3.01 Å) between one axial proton of the cyclohexenyl ring and a tetrachlorobenzendiolato ligand and (ii) a π-stacking interaction ($d_{\pi-\pi} \approx 3.67$ Å) between the benzyl fragment and a second tetrachlorobenzendiolato ligand (Figure 2, up).[15] Finally, in the solid state [**1**][*Δ*-(resp-*Λ*-TRISPHAT] does not present any symmetry plan and the C_4 atom become assymmetric in the global ion-pair. The interaction between $\mathbf{1}^+$ and *Δ*-(resp-*Λ*)-TRISPHAT is diastereoselective and results in the formation of a single diasteroisomer in the solid state over the four possible, and furthermore the couple of diastereoisomers [**1**][*Δ*-TRISPHAT] and [**1**][*Λ*-TRISPHAT] are enantiomers one from the other.

Solution NMR studies. The interactions displayed in solution between TRISPHAT and heptamethine dyes were studied by NMR spectroscopy. Initial experiments were carried in an NMR tube in $CDCl_3$ at room temperature between [**1**][Br] and

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increasing amounts of [cyn][Δ-TRISPHAT] (90% ee) (Figure 3). The NMR signals of the most easily distinguishable cyanine protons $H_5/H_{5'}$ and $H_6/H_{6'}$ belonging to the conjugated backbone are progressively shifted and splitted, indicating the establishment of a rapid equilibrium between [**1**][Δ-TRISPHAT] and [**1**][Br]. Finally, the ^{1}H NMR spectrum of isolated [**1**][Δ-TRISPHAT] (Figure 3e) clearly indicates a splitting of each resonance in two signals of equal intensity. This phenomenon is also observed in the ^{13}C spectra: all the signals split except those of the carbons C_1 and C_4 belonging to the symmetry plane of the molecule (see Figure S1 for ^{13}C spectrum).[16] These observations are in agreement with those observed in the solid state: Δ-TRISPHAT interacts selectively with the right side cavity inducing an asymmetry in the molecule; each vinylic proton $H_5/H_{5'}$ (resp $H_6/H_{6'}$) become magnetically non equivalent resulting in the apparition of two signals of equal intensity. The chemical shift difference $\Delta_{55'} = |\delta(H_5)-\delta(H_{5'})|$ (resp, $\Delta_{66'} = |\delta(H_6)-\delta(H_{6'})|$) of 0.03 and 0.06 ppm in chloroform-d_1 allows to quantify the strength of the supramolecular interaction. Furthermore interestingly, the magnitude of these chemical shift differentiation strongly increases in non-dissociating solvents and higher values were measured in benzene-d_6, $\Delta_{55'}$ = 0.09 ppm, $\Delta_{66'}$ = 0.29 ppm (Figure 4c). On the contrary, the splitting completely disappears in highly dissociating polar solvent like DMSO-d_6 (Figure S2). Such solvent effects have been frequently described in the literature for other systems and are the clear signature of a supramolecular ion-pairing effect in solution.[4,17]

In addition, ^{1}H NMR spectra of [**1**][Δ-TRISPHAT] (86% ee) and [**1**][*rac*-TRISPHAT] have also been recorded (Figure S3). Association with Λ-TRISPHAT results in a very similar splitting of the signals than that observed for Δ-TRISPHAT.[15] On the other hand, the ^{1}H NMR (and ^{13}C NMR) spectrum of [**1**][*rac*-TRISPHAT] shows only one set of signal like in the case of [**1**][Br], a result that can be again explained the rapid equilibrium between [**1**][Δ-TRISPHAT] and [[**1**][Λ-TRISPHAT] resulting in averaged NMR chemical shift.

In order to get more insight into this supramolecular ion-pairing effect, the influence of the substituents of **1**$^+$ on the association with Δ-TRISPHAT has been examined. Heptamethine dye **2**$^+$, featuring *n*-hexyl pendant groups instead of benzyl ones also present a splitting of the ^{1}H NMR signals when associating with Δ-TRISPHAT as shown Figure 4b. However, the differentiation is less pronounced than for **1**$^+$ ($\Delta_{55'}$ = 0.03 ppm, $\Delta_{66'}$ = 0.13 ppm in benzene-d_6) and almost not observable in $CDCl_3$. In that case, the supramolecular association is weaker, underlining the role of the benzyl moieties in the recognition process, as already observed in the solid state (Figure 2). Finally, the role of the ^{t}Bu fragment at the C_4 position as been examined. Ion-pairing formation also occurs between Δ-TRISPHAT and dye **3**$^+$, containing benzyl groups but no more ^{t}Bu fragment (Figure 1) as evidenced by thin-layer chromatography. But, by NMR, no more signals splitting is observed even in non-dissociating solvents (Figure 4a). This result was expected since in **3**$^+$, the C_4 atom is substituted by two pairs of homotopic substituent; hence, **3**$^+$ presents two equivalents faces with a rapid conformation equilibrium and there is no possibility for the TRISPHAT to discriminate between them. These experiments emphasis the crucial role played by the ^{t}Bu fragment in **1**$^+$ or **2**$^+$ because it fixes the conformation of the central cyclohexenyl ring allowing the differentiation between the two faces of the molecule, and the additional role of the benzyl groups who reinforces the supramolecular interaction.

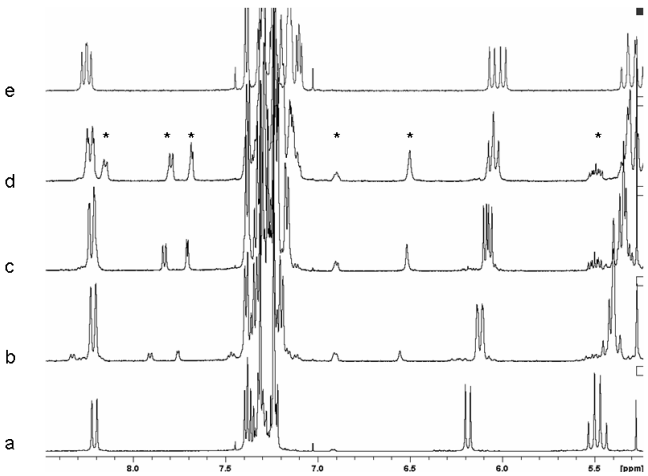

Fig. 3. Aromatic region of ^{1}H NMR ($CDCl_3$, TA, 500 MHz) of [**1**][Br] with increasing quantities of [cyn][Δ-TRISPHAT] a: 0 eq., b : 0.25 eq., c : 0.5 eq., d : 0.75 eq. e : 1 eq. (*, NMR signal of cyn).

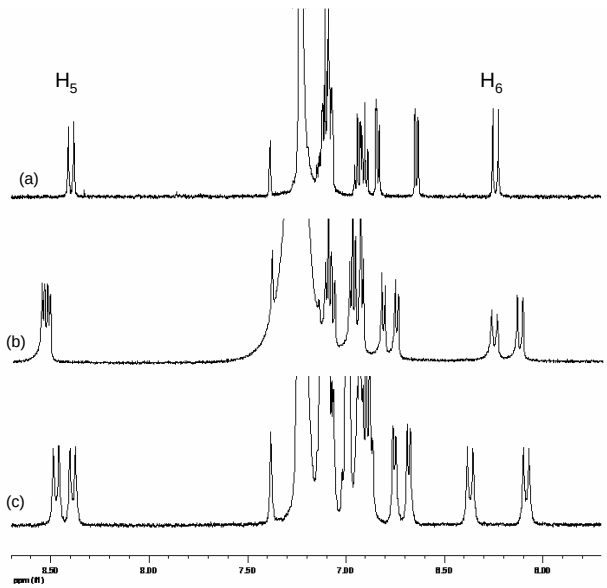

Fig. 4. Aromatic region of ^{1}H NMR spectra (benzene-d_6, RT, 500 MHz) of (a) [**3**][Δ-TRISPHAT], (b) [**2**][Δ-TRISPHAT] and (c) [**1**][Δ-TRISPHAT].

Concluding remarks.

We present in this paper a novel case of association using enantiopure TRISPHAT. Contrary to previous cases in which shorter monomethine dyes presented an helicoidal axis of chirality,[13a,18,19] the studied heptamethine dyes **1**$^+$, **2**$^+$ and **3**$^+$ featuring a fused cyclohexenyl ring does not present any chirality element due to the longer distances between the

terminal indolenine groups. However, in the case of **1**$^+$ and **2**$^+$ the conformation of the cyclohexenyl moieties is constrained by the thermodynamically favoured equatorial position of the *ter*-butyl fragment. As a consequence, the faces of the molecules become diastereotopic. The X-ray structure indicates that, *Δ*- (resp. *Λ*-) TRISPHAT interacts preferentially in the solid state with the right (resp. left) cavity defined by the cyclohexenyl ring and the distal benzyl substituant (Figure 1). This diastereoselective shape interaction breaks the planar symmetry of the supramolecule and the C_4 atom is now asymmetric resulting in the formation of a single diastereoisomer. Importantly, an identical diastereoselective ion-pairing interaction is observed in solution in non-dissociating solvents inducing an asymmetry of the molecule as illustrated by the splitting of the NMR signals. It is worth noting that the interaction between **1**$^+$ and enantiopure TRISPHAT leads to the formation of a single diastereoisomer over the four possible clearly underlining the high selectivity of the supramolecular interaction. Finally, the nature of the distal substituents (benzyl vs n-hexyl) defining the two cavities control the strength of this interaction: the more rigid benzyl fragment, allowing additional π–π stacking interactions with TRISPHAT induces the strongest interaction. These results contribute to expand the utilization scope of TRISPHAT ion: it is able to induce strong ion-pairing effect with non chiral molecule and to "reveal" the chirality of a *pro*-chiral compound.

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Experimental section.

All reactions were routinely performed under argon. NMR spectra were recorded at room temperature on a BRUKER AC 500 operating at 499.84 MHz for ^{1}H NMR and on a BRUKER AC 200 operating at 125.8 MHz and for ^{13}C and 81.91 for ^{31}P respectively . Data are listed in parts per million (ppm). UV-visible spectra were recorded on a Jasco V-550 spectrophotometer in diluted dichloromethane (resp. toluene) solution (*ca*. 10^{-5} mol.L^{-1}). Elemental analysis were performed by the Service Central d'Analyse du CNRS (Vernaison, France). Column Chromatography was performed on Merck Gerduran 60 (40-63 μm) silica using dichloromethane as eluent.

General Procedure for anion substitution:

[1-3][Br] (1 eq.) was dissolved in DCM (25 mL). [cyn][TRISPHAT] (1 eq.) was added and the solution was stirred 30 mn at room temperature. The solution was washed with water (3x15 mL), filtrated trough a silica plug (washed with DCM), and dried over Na_2SO_4. Then the solvents were evaporated to afford a green solid.

[1][*Δ*-TRISPHAT]. yield 85%; ^{1}H NMR (499.84 MHz, $CDCl_3$): δ 0.85 (s, 9H), 1.31 (m, 1H), 1.72 (s, 6H), 1.73 (s, 3H) 1.74 (s, 3H), 1.80 (dd, ^3J = 10 Hz, ^2J = 10 Hz, 1H), 1.85 (dd, ^3J = 10 Hz, ^2J = 10 Hz, 1H), 2.50 (m, 2H), 5.16 (d, ^2J = 17 Hz, 1H), 5.26 (d, ^2J = 17 Hz, 1H), 5.30 (d, ^2J = 17 Hz, 1H), 5.36 (d, ^2J = 17 Hz, 1H), 5.99 (d, ^3J = 15 Hz, 1H), 6.05 (d, ^3J = 15 Hz, 1H), 7.1-7.5 (m, 18H), 8.24 (d, ^3J = 15 Hz, 1H), 8.26 (d, ^3J = 15 Hz, 1H). ^{13}C NMR (50.32 MHz, $CDCl_3$): 27.5, 27.6, 28.5, 28.6, 32.5, 42.1, 48.5, 48.6, 49.7, 49.8, 102.0, 102.1, 111.0, 111.3, 114.1, 114.2, 122.7, 125.9, 126.0, 126.5, 126.6, 128.3, 128.4, 128.7, 128.8, 129.2, 129.7, 134.1, 141.0, 142.3, 142.7, 142.8, 145.1, 145.3, 151.7, 173.0, 173.3. ^{31}P NMR (91 MHz, $CDCl_3$): δ -80.7. Anal. calcd. for $C_{66}H_{60}N_20_{10}PCl_{13}$: C, 51.71, H, 3.94, N, 1.83, Found C, 51.74, H, 3.52, N, 1.71. UV-Vis (CH_2Cl_2): λ_{max} = 791 nm (ε_{max} = 320000 L.mol^{-1}.cm^{-1}).

[1][*Λ*-TRISPHAT]. ^{1}H NMR (499.84 MHz, $CDCl_3$): δ 0.85 (s, 9H), 1.31 (m, 1H), 1.72 (s, 6H), 1.73 (s, 3H) 1.74 (s, 3H), 1.80 (dd, ^3J = 10 Hz, ^2J = 10 Hz, 1H), 1.85 (dd, ^3J = 10 Hz, ^2J = 10 Hz, 1H), 2.49 (m, 2H), 5.16 (d, ^2J = 17 Hz, 1H), 5.26 (d, ^2J = 17 Hz, 1H), 5.30 (d, ^2J = 17 Hz, 1H), 5.36 (d, ^2J = 17 Hz, 1H), 6.00 (d, ^3J = 15 Hz, 1H), 6.03 (d, ^3J = 15 Hz, 1H), 7.1-7.5 (m, 18H), 8.24 (d, ^3J = 15 Hz, 1H), 8.26 (d, ^3J = 15 Hz, 1H).

[1][*rac* -TRISPHAT]. ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 0.84 (s, 9H), 1.30 (m, 1H), 1.71 (s, 6H), 1.73 (s, 6H), 1.86 (dd, ^3J = 13 Hz, ^2J = 13 Hz, 2H), 2.50 (dd, ^3J = 2 Hz, ^2J = 13 Hz, 2H), 5.23 (d , ^2J = 16 Hz, 2H), 5.29 (d, ^2J = 16 Hz, 2H), 6.01 (d, ^3J = 14 Hz, 2H), 7.2-7.5 (m, 18H), 8.25 (d, ^3J = 14 Hz, 2H).^{13}C NMR (50.32 MHz, $CDCl_3$): δ 27.4, 28.5, 28.6, 32.4, 42.1, 48.6, 49.7, 102.0, 111.2, 114.1, 122.6, 122.7, 125.9, 126.5, 128.4, 128.8, 129.3,129.7, 134.1, 141.0, 142.2, 142.8, 145.2, 151.6, 173.1.

[2][*Δ*-TRISPHAT]. yield = 80%; ^{1}H NMR (499.84 MHz, $CDCl_3$): δ 0.85 (t, ^3J = 8 Hz, 6H), 1.03(s, 9H), 1.30-1.60 (m, 18H), 1.70 (s, 12H), 1.80-1.90 (m, 4H), 2.1-2.3 (m, 2H), 2.80 (dd, ^3J = 2 Hz, ^2J = 10 Hz, 2H), 3.9-4.1 (m, 2H), 6.05 (m, 2H), 7.09 (d, ^3J = 8 Hz, 2H) 7.3-7.4 (m, 6H), 8.35 (d, ^3J = 15 Hz, 2H). ^{31}P NMR (91 MHz, $CDCl_3$): δ -80.9. Anal. calcd for $C_{64}H_{50}N_20_9PCl_{13}$: C, 52.40, H, 4.53, N, 1.91, Found C, 52.27, H, 4.39, N, 1.78. UV-Vis (CH_2Cl_2): λ_{max} = 786 nm (ε_{max} = 290000 L.mol^{-1}.cm^{-1}).

[3][*Δ*-TRISPHAT]. yield = 80%; ^{1}H NMR (499.84 MHz, $CDCl_3$): δ 1.61 (m, 2H), 1.75 (s, 12H), 2.2-2.4 (m, 4H), 5.20 (d , ^2J = 17 Hz, 2H), 5.31 (d, ^2J = 17 Hz, 2H), 6.07 (d, ^3J = 15 Hz, 2H), 7.04 (d, ^3J = 8 Hz, 2H), 7.1-7.3 (m, 16H), 7.38 (d, ^3J = 8 Hz, 2H), 8.29 (d, ^3J = 15 Hz, 2H). ^{31}P NMR (91 MHz, $CDCl_3$): δ -80.7. Anal. calcd for $C_{62}H_{48}N_20_8PCl_{13}$: C, 51.68, H, 3.36, N, 1.94, Found C, 51.97, H, 3.42, N, 1.77. UV-Vis (CH_2Cl_2): λ_{max} = 794 nm (ε_{max} = 290000 L.mol^{-1}.cm^{-1}).

Notes and references

a University of Lyon, ICL, CNRS - Ecole Normale Supérieure de Lyon, Laboratoire de Chimie, UMR 5182, 46 allée d'Italie, 69007 Lyon, France. olivier.maury@ens-lyon.fr.

Electronic Supplementary Information (ESI) available : cif file for compound [**1**][*rac*-TRISPHAT], CCDC 717753; supplementary crystallographic information and crystal packing description, additionnal NMR spectra (Figure S1, S2 and S3).

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