Diastereoselective supramolecular ion-pairing between the TRISPHAT anion and *pro*-chiral heptamethine cyanine dyes†

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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-ray diffraction and in solution by NMR spectroscopy. The presence of the conformationally restricted *tert*-butyl functionalized 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.

Introduction

Since its discovery in 1997 by Lacour and co-workers[1] and its large scale resolution,[2] the enantiopure TRISPHAT anion (tris(tetrachlorobenzenediolato)phosphate, Fig. 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-reagent for the enantiodifferentiation of cations,[4] as a chiral inducer onto labile cations[5] and as a chiral auxiliary for ion-pair mediated resolution properties by preferential extraction or chromatography.[3,6] Owing to these very special properties and to the quite easy synthesis and resolution, the TRISPHAT anion is now largely disseminated in the scientific community and is becoming a classical resolution auxiliary for many groups around the world.[7] During the course of our research aiming at the design of chromophores for nonlinear optical (NLO) applications, we fortunately discovered that the strong lipophilic character of the TRISPHAT anion, which is 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 chromophore concentrations of 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 cameras against damage caused by high-energy laser illumination but remain 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 the 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-ray diffraction analysis and NMR spectroscopy.

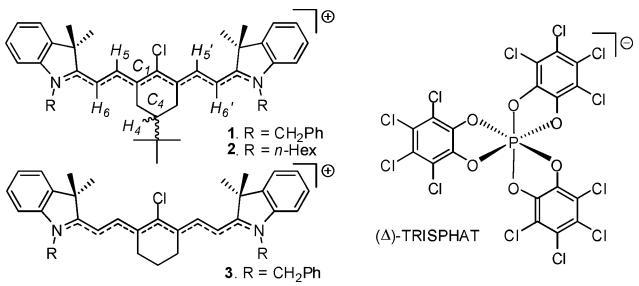

Fig. 1 Structures of the studied molecules.

Results and discussion

Synthesis

The cyanine dyes studied in this article (Fig. 1) differ by the functionalisation (or not) of the central cyclohexenyl ring by a *tert*-butyl 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 atom skeleton. 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 single and double bonds.[10,11] As a result, the three molecules present a symmetry plane containing the Cl, C_1,

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† Electronic supplementary information (ESI) available: Supplementary crystallographic information and crystal packing description, additional NMR spectra (Fig. S1, S2 and S3); cif file for compound [**1**][*rac*-TRISPHAT]. CCDC 717753. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/b905366b

C_4 and H_4 atoms (Fig. 1) and therefore their ^{1}H NMR spectra (Fig. 3a in the case [**1**][Br]) present a single set of signals for the two vinylic protons ($H_5/H_{5'}$ and $H_6/H_{6'}$, Fig. 1). It is worth noting that, owing to the presence of a symmetry plane, these dyes are not chiral, but the C_4 atom in compounds $\mathbf{1}^+$ and $\mathbf{2}^+$ 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]

Association of the cyanine dyes [**1–3**][X] (X = Br, I) with 90% ee [cin][*Δ*-TRISPHAT] (cin = cinchonidinium)[1,2] was carried out by mixing equivalent amounts of both salts in a 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 the 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 the TRISPHAT anion.[3,13] Compounds [**1–3**][*Δ*-TRISPHAT] were characterized by ^{1}H and ^{13}C NMR spectroscopy and gave satisfactory elemental analysis (see experimental section).

Solid state structure

Attempts to crystallize [**1**][*Δ*-TRISPHAT] (90% ee) by slow evaporation of a methanol–toluene solution resulted in the formation of a single crystal belonging to the centrosymmetric $P\bar{1}$ space group (N°2) of the racemate [**1**][*rac*-TRISPHAT] containing equal amounts 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 (Fig. 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 in the nine C(sp^2) carbon skeleton (overall tilt angle is 26°).[14] As expected for cyanine-like compounds, the conjugated backbone shows a "polyacetylene-type" structure 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 plane, Fig. 2): the face II contains the C_4 carbon and therefore the bulky ^{t}Bu fragment whereas the opposite face I is less sterically hindered. It is worth noting that the bulky TRISPHAT anion is located on this less sterically hindered face I (Fig. 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, Fig. 2), mirror images of each other. It is important to remark that the *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 tetrachlorobenzenediolato ligand and (ii) a π-stacking interaction ($d_{\pi\text{-}\pi} \approx 3.67$ Å) between the benzyl fragment and a second tetrachlorobenzenediolato ligand (Fig. 2, top).[15] Finally, in the solid state [**1**][*Δ*-(resp, *Λ*-)TRISPHAT] does not present any symmetry plane and the C_4 atom becomes asymmetric 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 diastereoisomer in the solid state out of the four possible, and furthermore the two diastereoisomers [**1**][*Δ*-TRISPHAT] and [**1**][*Λ*-TRISPHAT] are enantiomers of each other.

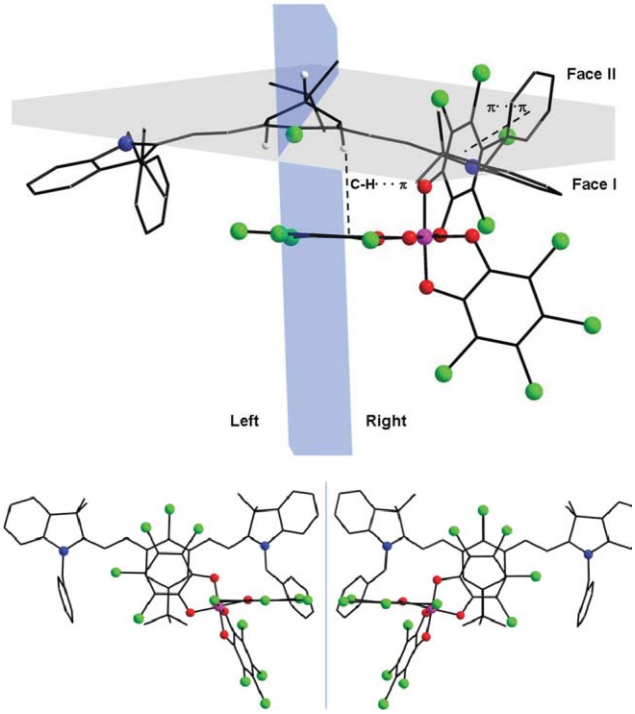

Fig. 2 X-Ray structure of [**1**][*rac*-TRISPHAT], H atoms were omitted for clarity except those involved in supramolecular interactions. (Top) representation of the two non-equivalent faces of the cyanine cation and the supramolecular interactions between $\mathbf{1}^+$ and *Δ*-TRISPHAT; (Bottom) representation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

Solution NMR studies

The interactions displayed in solution between TRISPHAT and heptamethine dyes were studied by NMR spectroscopy. Initial experiments were carried out in an NMR tube in $CDCl_3$ at room temperature between [**1**][Br] and increasing amounts of [cin][*Δ*-TRISPHAT] (90% ee) (Fig. 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 split, 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] (Fig. 3e) clearly indicates a splitting of each resonance into two signals of equal intensity. This phenomenon is also observed in the ^{13}C spectra: all the signals are split except those of the carbons C_1 and C_4 belonging to the symmetry plane of the molecule (see Fig. S1

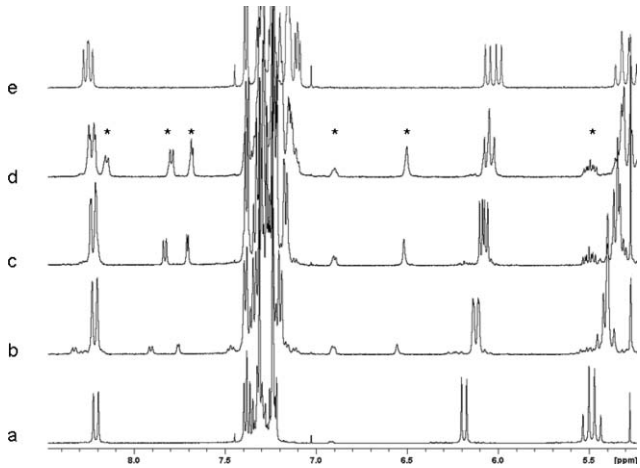

Fig. 3 Aromatic region of the ^{1}H NMR spectra ($CDCl_3$, RT, 500 MHz) of [**1**][Br] with increasing quantities of [cin][*Δ*-TRISPHAT]; a: 0 eq., b: 0.25 eq., c: 0.5 eq., d: 0.75 eq., e: 1 eq. (*, NMR signal of cin).

for ^{13}C spectrum, ESI†).[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, $H_6/H_{6'}$) becomes magnetically non-equivalent resulting in the appearance of two signals of equal intensity. The chemical shift differences $\Delta_{55'} = |\delta(H_5) - \delta(H_{5'})|$ (resp, $\Delta_{66'} = |\delta(H_6) - \delta(H_{6'})|$) of 0.03 and 0.06 ppm in chloroform-d_1 allow quantification of the strength of the supramolecular interaction. Furthermore interestingly, the magnitude of these chemical shift differentiations 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 (Fig. 4c). On the contrary, the splitting completely disappears in a highly dissociating polar solvent like DMSO-d_6 (Fig. S2, ESI†). 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]

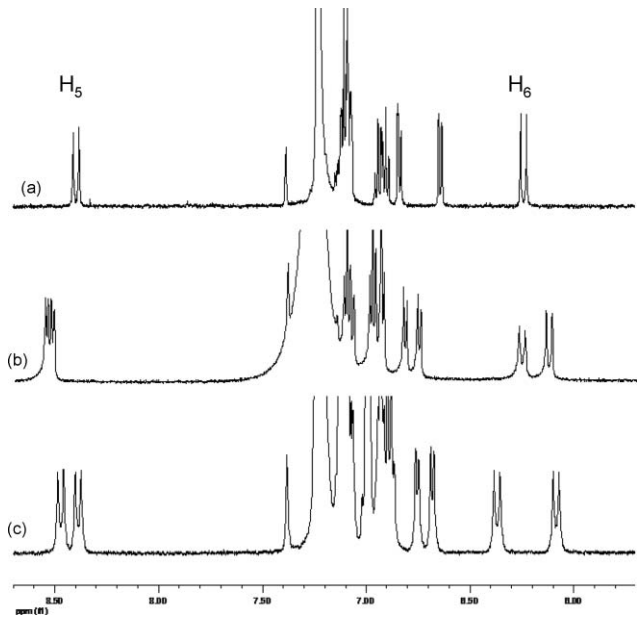

Fig. 4 Aromatic region of ^{1}H NMR spectra (benzene-d_6, RT, 500 MHz) of (a) [**3**][*Δ*-TRISPHAT], (b) [**2**][*Δ*-TRISPHAT] and (c) [**1**][*Δ*-TRISPHAT].

In addition, ^{1}H NMR spectra of [**1**][*Λ*-TRISPHAT] (86% ee) and [**1**][*rac*-TRISPHAT] have also been recorded (Fig. S3, ESI†). Association with *Λ*-TRISPHAT results in a very similar splitting of the signals to 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 again be explained by 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 $\mathbf{1}^+$ on the association with *Δ*-TRISPHAT has been examined. Heptamethine dye $\mathbf{2}^+$, featuring *n*-hexyl pendant groups instead of benzyl groups also presents a splitting of the ^{1}H NMR signals when associating with *Δ*-TRISPHAT as shown in Fig. 4b. However, the differentiation is less pronounced than for $\mathbf{1}^+$ ($\Delta_{55'} = 0.03$ ppm, $\Delta_{66'} = 0.13$ ppm in benzene-d_6) and almost not observable in $CDCl_3$. In this case, the supramolecular association is weaker, underlining the role of the benzyl moieties in the recognition process, as already observed in the solid state (Fig. 2). Finally, the role of the ^{t}Bu fragment at the C_4 position has been examined. Ion-pairing formation also occurs between *Δ*-TRISPHAT and dye $\mathbf{3}^+$, containing benzyl groups but no ^{t}Bu fragment (Fig. 1) as evidenced by thin-layer chromatography. But, by NMR, no more signal splitting is observed, even in non-dissociating solvents (Fig. 4a). This result was expected since in $\mathbf{3}^+$ the C_4 atom is substituted by two homotopic substituents; hence, $\mathbf{3}^+$ presents two equivalents faces with a rapid conformation equilibrium and there is no possibility for the TRISPHAT to discriminate between them. These experiments emphasise the crucial role played by the ^{t}Bu fragment in $\mathbf{1}^+$ or $\mathbf{2}^+$ 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 reinforce the supramolecular interaction.

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 a helicoidal axis of chirality,[13a,18,19] the studied heptamethine dyes $\mathbf{1}^+$, $\mathbf{2}^+$ and $\mathbf{3}^+$ featuring a fused cyclohexenyl ring do not present a chirality element due to the longer distances between the terminal indolenine groups. However, in the cases of $\mathbf{1}^+$ and $\mathbf{2}^+$ the conformation of the cyclohexenyl moieties is constrained by the thermodynamically favoured equatorial position of the *tert*-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 substituent (Fig. 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 $\mathbf{1}^+$ and enantiopure

TRISPHAT leads to the formation of a single diastereoisomer out of 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 controls 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 the TRISPHAT ion: it is able to induce a strong ion-pairing effect with a non-chiral molecule and to "reveal" the chirality of a *pro*-chiral compound.

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 NMR and 81.91 for ^{31}P NMR 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 analyses 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). [cin][TRISPHAT] (1 eq.) was added and the solution was stirred for 30 min at room temperature. The solution was washed with water (3 × 15 mL), filtered through 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, ^{3}J = 10 Hz, ^{2}J = 10 Hz, 1H), 1.85 (dd, ^{3}J = 10 Hz, ^{2}J = 10 Hz, 1H), 2.50 (m, 2H), 5.16 (d, ^{2}J = 17 Hz, 1H), 5.26 (d, ^{2}J = 17 Hz, 1H), 5.30 (d, ^{2}J = 17 Hz, 1H), 5.36 (d, ^{2}J = 17 Hz, 1H), 5.99 (d, ^{3}J = 15 Hz, 1H), 6.05 (d, ^{3}J = 15 Hz, 1H), 7.1–7.5 (m, 18H), 8.24 (d, ^{3}J = 15 Hz, 1H), 8.26 (d, ^{3}J = 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} = 320 000 L mol^{-1} cm^{-1}).

[1]|[*Δ*-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, ^{3}J = 10 Hz, ^{2}J = 10 Hz, 1H), 1.85 (dd, ^{3}J = 10 Hz, ^{2}J = 10 Hz, 1H), 2.49 (m, 2H), 5.16 (d, ^{2}J = 17 Hz, 1H), 5.26 (d, ^{2}J = 17 Hz, 1H), 5.30 (d, ^{2}J = 17 Hz, 1H), 5.36 (d, ^{2}J = 17 Hz, 1H), 6.00 (d, ^{3}J = 15 Hz, 1H), 6.03 (d, ^{3}J = 15 Hz, 1H), 7.1–7.5 (m, 18H), 8.24 (d, ^{3}J = 15 Hz, 1H), 8.26 (d, ^{3}J = 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, ^{3}J = 13 Hz, ^{2}J = 13 Hz, 2H), 2.50 (dd, ^{3}J = 2 Hz, ^{2}J = 13 Hz, 2H), 5.23 (d, ^{2}J = 16 Hz, 2H), 5.29 (d, ^{2}J = 16 Hz, 2H), 6.01 (d, ^{3}J = 14 Hz, 2H), 7.2–7.5 (m, 18H), 8.25 (d, ^{3}J = 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, ^{3}J = 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, ^{3}J = 2 Hz, ^{2}J = 10 Hz, 2H), 3.9–4.1 (m, 2H), 6.05 (m, 2H), 7.09 (d, ^{3}J = 8 Hz, 2H), 7.3–7.4 (m, 6H), 8.35 (d, ^{3}J = 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} = 290 000 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, ^{2}J = 17 Hz, 2H), 5.31 (d, ^{2}J = 17 Hz, 2H), 6.07 (d, ^{3}J = 15 Hz, 2H), 7.04 (d, ^{3}J = 8 Hz, 2H), 7.1–7.3 (m, 16H), 7.38 (d, ^{3}J = 8 Hz, 2H), 8.29 (d, ^{3}J = 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} = 290 000 L mol^{-1} cm^{-1}).

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