

Large-Size Star-Shaped Conjugated (Fused) Triphthalocyaninehexaazatriphenylene

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ABSTRACT: Star-shaped triphthalocyaninehexaazatriphenylene 1 was synthesized via condensation between a new building block 1,2-diaminophthalocyanine and cyclohexanehexaone. Compound 1 represents the largest star-shaped phthalocyanine-fused hexaazatriphenylene reported so far. This largely expanded phthalocyanine shows good solubility and has a strong tendency to aggregate in both solution and on surface, indicating its potential as active component in organic electronic devices.

Linear and star-shaped molecules based on π -conjugated chromophores containing a polycyclic aromatic core, with the adequate HOMO and LUMO energy orbitals,¹ have generated significant interest for use in optoelectronic devices² due to their properties of isotropic absorption and strong tendency to stack into quasi-1D columns, thus generating a preferred charge transporting pathway.³

The majority of organic semiconductors display hole-transporting properties (p-type),⁴ being the phthalocyanines (Pcs) one of the most representative families. Pcs are robust heteroaromatic macrocycles renowned for their intense absorption in the visible and near infrared spectrum.⁵ Among all their interesting features, it is possible to highlight that their properties can be tuned by introducing suitable substituents in peripheral and axial positions,⁶ and the presence of electron donor groups attached to the isoindole rings gives them p-type semiconducting character. Their extensive π -conjugated planar system promotes their ordering by π - π stacking and, in addition, their reorganization energy is low.⁷ On the other hand, materials capable of electron transport (n-type) based on fullerenes, perylene diimides and perfluorinated compounds have also been developed.⁸ Recently, 1,4,5,8,9,12-hexaazatriphenylenes (HAT) and some expanded derivatives have emerged as n-type materials that, when properly substituted, organize themselves into columnar structures.⁹ Finally, even more interesting and novel materials are ambipolar compounds, capable of transporting electrons and holes at the same time, which can be applied to organic field effect transistors (OFETs) and organic light emitting field effect transistors (OLETs).¹⁰

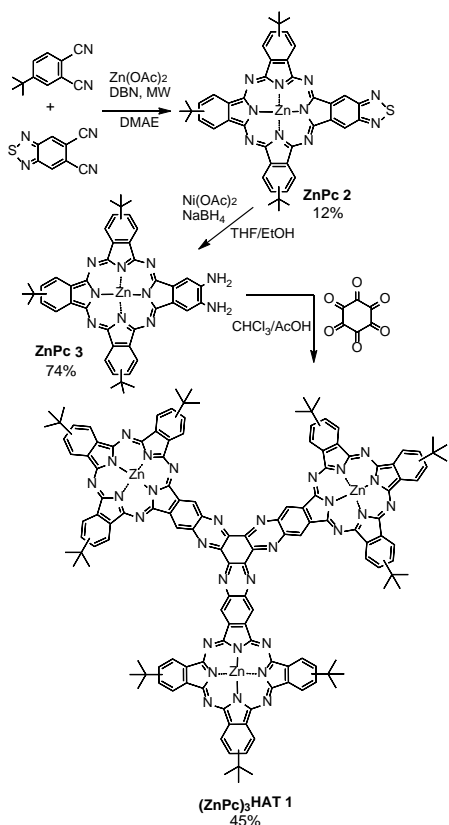
Donor-acceptor systems formed by electron-rich groups conjugated with electron-poor moieties that can organize themselves into columns, are good candidates to show ambipolar behavior.¹¹ For this reason, the fusion of p-type phthalocyanines with some other n-transporting materials might give rise to different grade of conjugation between both systems

affording potential candidates for ambipolar character. The synthesis of this type of systems has been scarcely described to date due to the difficulties to synthesize phthalocyanines with the adequate substituents for the condensation with acceptor moieties. Just one example has been published recently where a Pc is fused to a perylene through a benzimidazole ring.¹² However, the synthesis of Pcs conjugated with HAT has not been achieved yet.

Herein, we report a large-size star-shaped donor-acceptor system that presents a hexaazatriphenylene group fused with three phthalocyanine units, (ZnPc)₃HAT **1** (Scheme 1). This star-shaped chromophore was synthesized and characterized, and its optical and electrochemical properties were investigated. Compound **1** presents strong tendency to aggregate in both solution and on surface, indicating their potential applications for organic electronic devices.

Triad (ZnPc)₃HAT **1** is obtained by condensation of *o*-diamino ZnPc **3** with cyclohexane-1,2,3,4,5,6-hexaone.¹³ Many aminoPcs have been synthesized,¹⁴ however the ZnPc **3** has not been described to date. Since the free amino groups are incompatible with phthalonitrile cyclotetramerization reaction, we had to find either a suitable protecting group or a synthon for the *o*-diamine moiety. The second option was selected with the use of the 2,1,3-thiadiazole group,¹⁵ whose electron-withdrawing character would favour the cyclization reaction and further it can be easily reduced to an *o*-diamino group. The cyclotetramerization of 5,6-dicyano-2,1,3-benzothiadiazole¹⁶ and 4-*tert*-butylphthalonitrile in the presence of zinc acetate yielded ZnPc **2** in 12%, a remarkable yield for this kind of statistical condensations. The reaction with NaBH₄ in the presence of nickel boride,¹⁷ prepared *in situ* from nickel (II) acetate, afforded ZnPc **3** in 72%. Condensation of the latter with cyclohexane-1,2,3,4,5,6-hexaone gave rise to the (ZnPc)₃HAT **1** in 45% yield.

Scheme 1. Synthesis of (ZnPc)₃HAT **1**.



All new compounds were characterized by ^1H NMR, UV-Vis, FT-IR and high resolution mass spectrometry (see ESI). ZnPc **2** and ZnPc **3** present very well resolved ^1H NMR spectra in THF- d_8 as solvent. The ^1H NMR spectrum of ZnPc **2** in THF (Figure 1) shows two multiplets at 9.50-8.93 and 8.37-8.14 ppm corresponding to the aromatic hydrogens of the t -Bu-substituted rings and the two hydrogen atoms in the neighborhood of the thiadiazole ring. In the ^1H NMR spectrum of ZnPc **3** two new multiplets appear at 8.57 ppm, which corresponds to the two hydrogen atoms in the neighborhood of the amino groups, and at 4.95 ppm, corresponding to the amino groups. The aliphatic region of the spectrum, which is equal for both ZnPcs, only contains the intense signal of the *tert*-butyl groups (See ESI, Fig S6). Although (ZnPc) $_3$ HAT **1** is a mixture of regioisomers and shows an extremely high degree of planarity and a pronounced tendency to π - π stacking, even using THF- d_8 as solvent, which yields a worse resolved spectrum than in the case of phthalocyanines **2** and **3**, its ^1H NMR spectrum confirms undoubtedly the structure, showing the presence of two different types of multiplets at 8.11-8.45 and 9.39-9.59 ppm corresponding to the aromatic protons (See ESI, Fig. S7). The existence of **1** is also demonstrated by high resolution MS by the peak at m/z 2383.779 (See ESI, Fig. S8).

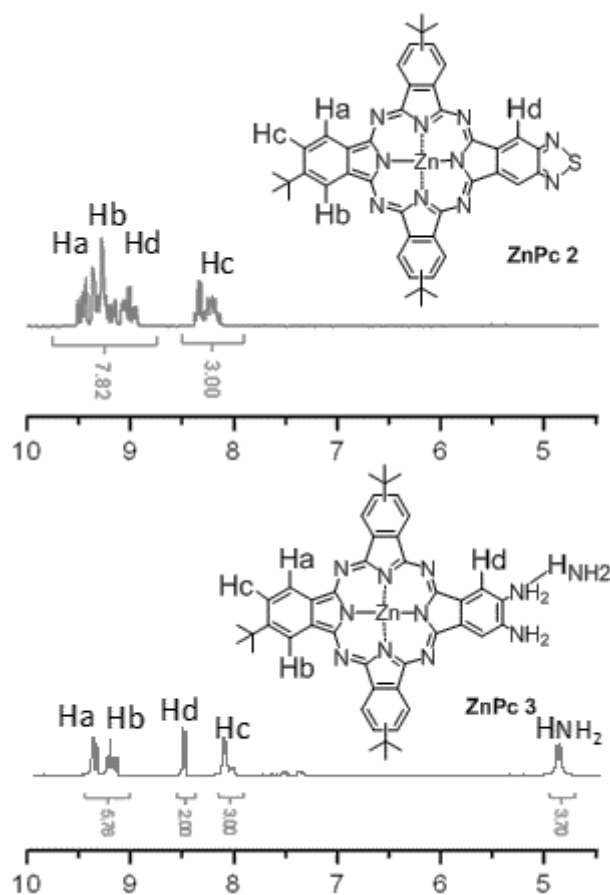


Figure 1. NMR in THF- d_8 of ZnPc **2** and ZnPc **3**.

The UV-Vis spectra of ZnPcs **1-3** using THF as a solvent are depicted in Figure 2. The splitting of 38 nm in the Q band of the ZnPc **2** spectrum is quite remarkable, being attributed to the acceptor character of the thiadiazolo fused ring. In case of ZnPc **3** there is no splitting in the Q band due to the presence of the electron donating amino groups. For both Pcs the absorption maxima in the Q band are located at 680 nm. The UV-Vis spectrum of the

(ZnPc)₃HAT **1** is completely different from the previous ones. The intensity of the Q band is much lower as a result of the above-mentioned strong aggregation. Moreover, the bathochromic shift of 18 nm and the broad profile, with absorption from 700 to 900 nm, points out to some degree of conjugation between the HAT core and the peripheral Pc subunits.

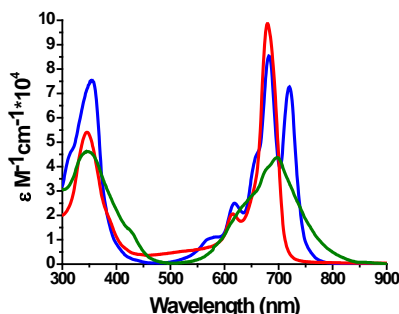


Figure 2. UV-Vis spectra in THF solution of ZnPc **2** (blue line), ZnPc **3** (red line) and (ZnPc)₃HAT **1** (green line).

Cyclic voltammetry studies were carried out in a dry PhCN solution with 0.1 M TBAPF₆ as supporting electrolyte (See Table 1 and ESI, Fig. S9). ThiadiazoloZnPc **2** presents three reduction peaks at -1.04, -1.19 and -1.37 V (*vs* SCE), corresponding the first and second one to the thiadiazole ring and the third one to the phthalocyanine, and two oxidation potentials at 0.40 and 0.58 V (*vs* SCE). On the other hand, a cathodic shift, as expected, is observed in the first oxidation peak of the diamino ZnPc **3**, appearing at 0.30 V, while an anodic shift for the second oxidation potential, appearing at 0.71 V, occurs. In the case of the (ZnPc)₃HAT **1**, the first oxidation potential appears at 0.39 V, indicating again the interaction between the subunits. Also two reduction peaks are observed for **1**, the first one at -1.10 V corresponding to the HAT moiety and the other at -1.42 V corresponding to the Pc ring.

The frontier orbitals of **1-3** were calculated from the electrochemical oxidation and reduction potentials. The HOMO and the LUMO potentials for the (ZnPc)₃HAT **1** were determined to be approximately -5.42 and -3.6 eV. The energy values suggest that it is a good candidate for ambipolar field-effect transistors.

Table 1. Redox potentials (*vs* SCE) in deaerated PhCN

Compound	E_{ox}^1	E_{ox}^2	E_{red}^1	E_{red}^2	E_{red}^3	HOMO	LUMO
ZnPc 2	0.40	0.58	-	-	-	-5.34	-3.12
ZnPc 3	0.30	0.71	1.04	1.19	1.37	-4.90	-3.33
(ZnPc) ₃ HAT 1	0.39	---	1.31	-	---	-5.42	-3.6
			1.10	1.42			

The deposition of functional molecules on surfaces is often required to move towards potential applications. Therefore, we investigated here the self-assembly of **1** when a 10^{-4} M solution of this molecule in THF is drop-casted on SiO_2 surface. In figure 3(top) the Atomic Force Microscopy (AFM) topographic images acquired are shown. Clearly, aggregates formed by small fibers could be observed. After exposing such surface aggregates to vapors of CH_2Cl_2 , the formation of longer fibers with typical heights of the order of 2.5 nm can be seen (Figure 3, bottom). These results elucidate the high tendency of this molecular system to form nanostructures driven by the π - π interactions.

In summary, a hexaazatriphenylenetriphthalocyaninate zinc has been prepared for the first time by an efficient synthetic method, which implies a triple condensation reaction between an unsymmetrical diamino ZnPc derivative and cyclohexanehexaone. Uv-vis and AFM studies have demonstrated that $(\text{ZnPc})_3\text{HAT}$ **1** has a strong tendency to aggregate in both solution and on surface, indicating its potential as active component in organic electronic devices. New derivatives with different substitution in the phthalocyanine core are underway in order to get a new family of donor-acceptor systems organized in one-dimensional columnar phases.

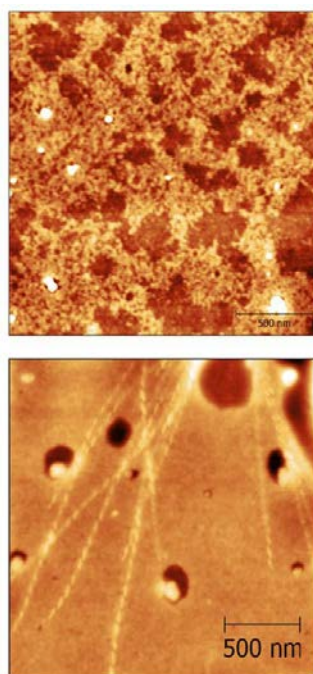


Figure 3. AFM topographic images of the self-assemblies formed by drop-casting a 10^{-4} M solution of **1** on SiO_2 in THF: Top: without solvent annealing. Bottom: after annealing with CH_2Cl_2 vapors.

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