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Large-Size Star-Shaped Conjugated (Fused) Triphthalocyaninehexaazatriphenylene

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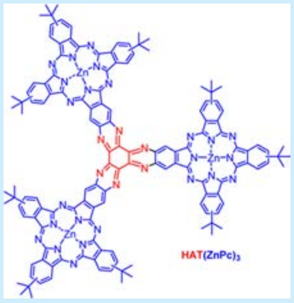
Supporting Information

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 both in solution and on the surface, indicating its potential as an active component in organic electronic devices.



Linear and star-shaped molecules based on π-conjugated chromophores containing a polycyclic aromatic core, with adequate HOMO and LUMO energy orbitals,[1] have generated significant interest for use in optoelectronic devices[2] 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] with the phthalocyanines (Pcs) being 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 $\pi-\pi$ stacking, and in addition, their reorganization energy is low.[7] On the other hand, materials capable of electron transport (n-type) based on fullerenes, perylenediimides, 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 for showing ambipolar behavior.[11] For this reason, the fussion of p-type phthalocyanines with some other n-transporting materials might give rise to different grades 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 adequate substituents for condensation with acceptor moieties. 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 a strong tendency to aggregate both in solution and on the 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 amino-Pcs 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 favor the cyclization reaction with the added benefit of being easily reduced to an *o*-diamino group. The

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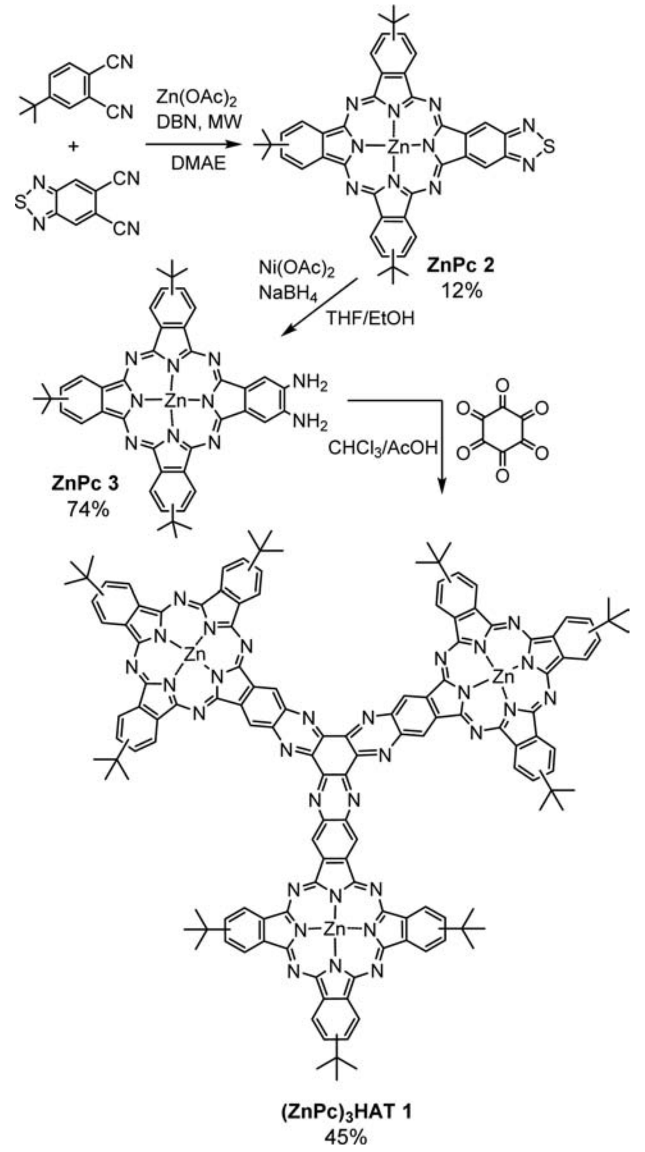
Scheme 1. Synthesis of $(ZnPc)_3$HAT 1



cyclotetramerization of 5,6-dicyano-2,1,3-benzothiadiazole[16] and 4-*tert*-butylphthalonitrile in the presence of zinc acetate gave ZnPc **2** in 12% yield, a remarkable yield for this kind of statistical condensation. The reaction with $NaBH_4$ in the presence of nickel boride,[17] prepared in situ from nickel(II) acetate, afforded ZnPc **3** in 74% yield. Condensation of the latter with cyclohexane-1,2,3,4,5,6-hexaone gave rise to the $(ZnPc)_3$HAT **1** in 45% yield.

All new compounds were characterized by ^{1}H NMR, UV–vis, FT-IR, and high resolution mass spectrometry [see Supporting Information (SI)]. ZnPc **2** and ZnPc **3** present very well resolved ^{1}H NMR spectra in THF-d_8 as solvent. The ^{1}H 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 ^{1}H 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 SI, Figure 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 when using THF-d_8 as solvent, which yields a less resolved spectrum than in the case of phthalocyanines **2** and **3**, its ^{1}H NMR spectrum undoubtedly confirms 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 SI, Figure S7). The existence of **1** is also demonstrated by high resolution MS by the peak at m/z 2383.779 (see SI, Figure S8).

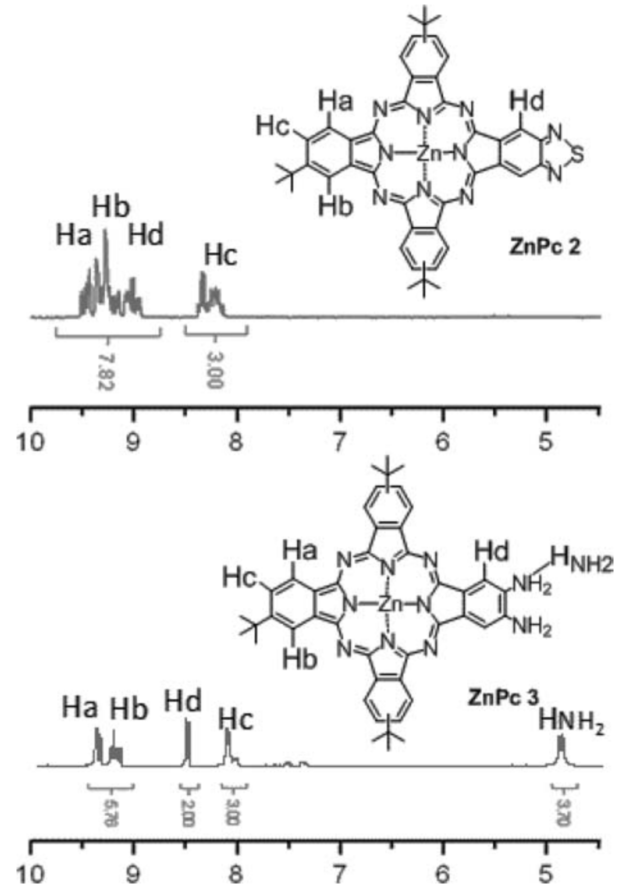


Figure 1. NMR in THF-d_8 of ZnPc **2** and ZnPc **3**.

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, as it is attributed to the acceptor character of the thiadiazolo fused ring. In the case of ZnPc **3** there is no splitting in the Q-band due to the presence of

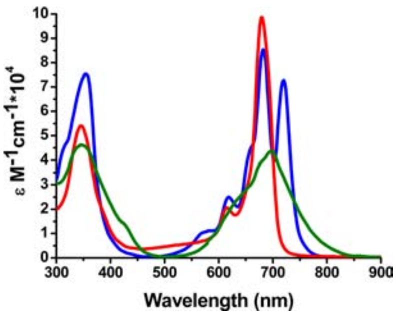


Figure 2. UV–vis spectra in THF solution of ZnPc **2** (blue line), ZnPc **3** (red line), and $(ZnPc)_3$HAT **1** (green line).

Table 1. Redox Potentials in V (vs SCE) in Deaerated PhCN

compd	E_{ox}^1	E_{ox}^2	E_{red}^1	E_{red}^2	E_{red}^3	HOMO	LUMO
ZnPc **2**	0.40	0.58	−1.04	−1.19	−1.37	−5.34	−3.12
ZnPc **3**	0.30	0.71	−1.31	–	–	−4.90	−3.33
$(ZnPc)_3HAT$ **1**	0.39	–	−1.10	−1.42	–	−5.42	−3.6

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 $(ZnPc)_3HAT$ **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, point out some degree of conjugation between the HAT core and the peripheral Pc subunits.

Cyclic voltammetry studies were carried out in a dry PhCN solution with 0.1 M $TBAPF_6$ as the supporting electrolyte (see Table 1 and SI, Figure S9). ThiadiazoleZnPc **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, appering 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.

The deposition of functional molecules on surfaces is often required to move toward 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 the 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 on 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 $(ZnPc)_3HAT$ **1** has a strong tendency to aggregate both in solution and on the surface, indicating its potential as an active component in organic electronic devices. New derivatives with different substitution in the phthalocyanine core are underway in order to obtain a new family of donor−acceptor systems organized in one-dimensional columnar phases.

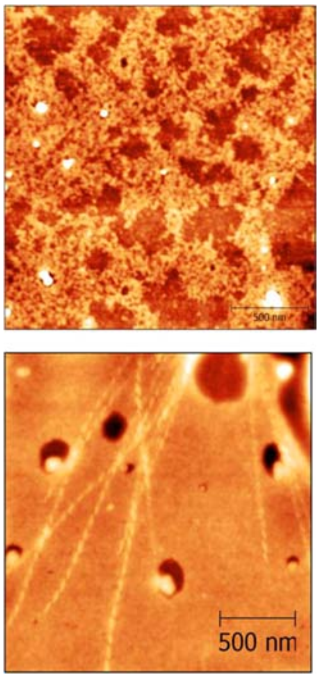


Figure 3. AFM topographic images of the self-assemblies formed by drop-casting a 10^{-4} M solution of **1** on SiO_2 in THF: (top) without solvent annealing; (bottom) after annealing with CH_2Cl_2 vapors.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00412.

Experimental procedures and characterization of new reported compounds (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Tang, M. L.; Reichardt, A. D.; Wei, P.; Bao, Z. *J. Am. Chem. Soc.* **2009**, *131*, 5264. (b) Moss, K. C.; Bourdakos, K. N.; Bhalla, V.;

Kamtekar, K. T.; Bryce, M. R.; Fox, M. A.; Vaughan, H. L.; Dias, F. B.; Monkman, A. P. *J. Org. Chem.* **2010**, *75*, 6771.

(2) (a) Mativetsky, J. M.; Kastler, M.; Savage, R. C.; Gentilini, D.; Palma, M.; Pisula, W.; Müllen, K.; Samorı, P. *Adv. Funct. Mater.* **2009**, *19*, 2486. (b) Gearba, R. I.; Lehmann, M.; Levin, J.; Ivanov, D. A.; Koch, M. H. J.; Barberá, J.; Debije, M. G.; Piris, J.; Geerts, Y. H. *Adv. Mater.* **2003**, *15*, 1614.

(3) (a) Forrest, S. R. *Nature* **2004**, *428*, 911. (b) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953.

(4) Hutchison, G.; Ratner, M.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 16866.

(5) (a) *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, 1990−1996; Vols. *1*−*4*. (b) McKeown, N. B. *Phthalocyanine Materials: Synthesis, Structure and Function*; Cambridge University Press: 1998. (c) Mack, J.; Kobayashi, N. *Chem. Rev.* **2011**, *111*, 281.

(6) (a) de la Torre, G.; Claessens, C. G.; Torres, T. *Chem. Commun.* **2007**, 2000. (b) Martin-Gomis, L.; Fernández-Lázaro, F.; Sastre-Santos, A. *J. Mater. Chem. A* **2014**, *2*, 15672.

(7) (a) Wang, H. B.; Zhu, F.; Yang, J. L.; Geng, G. H.; Yan, D. H. *Adv. Mater.* **2007**, *19*, 2168. (b) Huang, L. Z.; Liu, C. F.; Qiao, X. L.; Tian, H. K.; Geng, Y. H.; Yan, D. H. *Adv. Mater.* **2011**, *23*, 3455. (c) Norton, J. E.; Brédas, J. L. *J. Chem. Phys.* **2008**, *128*, 034701. (d) Zhang, Y.; Dong, H.; Tang, Q.; Ferdous, S.; Liu, F.; Mannsfeld, S. C. B.; Hu, W.; Briseno, A. L. *J. Am. Chem. Soc.* **2010**, *132*, 11580−11584.

(8) (a) Tonzola, C. J.; Alam, M. M.; Kaminsky, W.; Jenekhe, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 13548. (b) Chua, L.-L.; Zaumseil, J.; Chang, J.-F.; Ou, E.; Ho, P.; Sirringhaus, H.; Friend, R. *Nature* **2005**, *434*, 194. (c) Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066. (d) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. *Adv. Mater.* **2010**, *22*, 3876.

(9) (a) Wang, M.; Li, Y.; Tong, H.; Cheng, Y.; Wang, L.; Jing, X.; Wang, F. *Org. Lett.* **2011**, *13*, 4378. (b) Juárez, R.; Moreno Oliva, M.; Ramos, M.; Segura, J. L.; Alemán, C.; Rodríguez-Ropero, F.; Curcó, D.; Montilla, F.; Coropceanu, V.; Brédas, J. L.; Qi, Y.; Kahn, A.; Ruiz Delgado, M. C.; Casado, J.; López Navarrete, J. T. *Chem. - Eur. J.* **2011**, *17*, 10312. (c) Choudhary, S.; Gozalvez, C.; Higelin, A.; Krossing, I.; Melle-Franco, M.; Mateo-Alonso, A. *Chem. - Eur. J.* **2014**, *20*, 1525.

(10) (a) Zaumseil, J.; Sirringhaus, H. *Chem. Rev.* **2007**, *107*, 1296. (b) Lei, T.; Dou, J. H.; Ma, Z. J.; Yao, C. H.; Liu, C. J.; Wang, J. Y.; Pei, J. *J. Am. Chem. Soc.* **2012**, *134*, 20025. (c) Hayashi, H.; Nihashi, W.; Umeyama, T.; Matano, Y.; Seki, S.; Shimizu, Y.; Imahori, H. *J. Am. Chem. Soc.* **2011**, *133*, 10736−10739.

(11) (a) Geramita, K.; Tao, Y.; Segalman, R. A.; Tilley, T. D. *J. Org. Chem.* **2010**, *75*, 1871. (b) Ye, J.; Chen, Z.; Fung, M. K.; Zheng, C.; Ou, X.; Zhang, X.; Yuan, Y.; Lee, C. S. *Chem. Mater.* **2013**, *25*, 2630.

(12) Blas-Ferrando, V. M.; Ortiz, J.; Ohkubo, K.; Fukuzumi, S.; Fernández-Lázaro, F.; Sastre-Santos, Á. *Chem. Sci.* **2014**, *5*, 4785.

(13) Skujins, S.; Webb, G. A. *Tetrahedron* **1969**, *25*, 3935.

(14) (a) Kudrevich, S. V.; Ali, H.; van Lier, J. E. *J. Chem. Soc., Perkin Trans. 1* **1994**, *1*, 2767. (b) Sutton, J. M.; Boyle, R. W. *Chem. Commun.* **2001**, 2014. (c) González-Cabello, A.; Vázquez, P.; Torres, T.; Guldi, D. M. *J. Org. Chem.* **2003**, *68*, 8635. (d) Cong, F.-D.; Ning, B.; Du, X. G.; Ma, C. Y.; Yu, H. F.; Chen, B. *Dyes Pigm.* **2005**, *66*, 149. (e) Nombona, N.; Tau, P.; Sehlotho, N.; Nyokong, T. *Electrochim. Acta* **2008**, *53*, 3139.

(15) Neto, B. A. D.; Lapis, A. A. M.; da Silva, E. N.; Dupont, J. *Eur. J. Org. Chem.* **2013**, *2013*, 228.

(16) Burmester, C.; Faust, R. *Synthesis* **2008**, *2008*, 1179.

(17) Schlütter, F.; Wild, A.; Winter, A.; Hager, M. D.; Baumgaertel, A.; Friebe, C.; Schubert, U. S. *Macromolecules* **2010**, *43*, 2759.