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Using the commercially available 1,4,5,8-tetrachloroanthraquinone (**1**) as starting material, a N-heterocoronene derivative **3** was synthesized via a straightforward two-step reaction. Compound **3** shows a similar photostability as perylene dyes, qualifying it as a promising colorant.

Most organic colorants exhibit three characteristic features: (1) a conjugated carbon-rich framework, often aromatic units such as naphthalene,<sup>1</sup> (2) conjugated double bonds as occurring in azo dyes,<sup>2</sup> and (3) additional substituents, so-called auxochromic groups, for example carboximides.<sup>3</sup> Organic colorants have thus been categorized according to their chemical structures. From a commercial point of view, azo dyes dominate the markets with more than 60% due to their low production costs. The second most important organic chromophores are carbonyl based compounds, particularly anthraquinones.<sup>4</sup> Using functionalized anthraquinones as starting materials, even larger polycyclic pigments have been developed, such as quinacridone,<sup>5</sup> indanthrone,<sup>6</sup> flavanthrone,<sup>7</sup> and pyranthrone.<sup>8</sup> Another approach uses polycyclic aromatic hydrocarbons (PAHs) as core that is substituted by multiple carbonyls and groups containing lone pairs of electrons.<sup>9</sup> Typical examples for such chromophores are perylenecarboximide dyes,<sup>10</sup> which serve not only as conventional colorants but also as active components of organic photonics and electronics.<sup>11</sup> Alternative colorant structures are still in high demand.

## From anthraquinone to heterocoronene as stable red chromophore†

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Herein we combine coronene<sup>12</sup> (an even larger PAH than perylene) and four carboximides to achieve a new N-heterocoronene chromophore, namely 1,4,7,10-tetra(4-alkylphenyl)-1,4,7,10-tetraazacoronene-2,3,8,9-tetraone (alkyl is: *t*-butyl for **3a**, *n*-dodecyl for **3b**). Starting from a commercially available anthraquinone (**1**)<sup>13</sup> *i.e.* 1,4,5,8-tetrachloro-9,10-anthracenedione, **3** was synthesized by a simple two-step protocol (Scheme 1). A four-fold Buchwald-Hartwig amination between **1** and 4-alkylaniline, first, furnished the intermediate 1,4,5,8-tetrakis((4-alkylphenyl)amino)anthracene-9,10-dione (**2**). Then, a microwave-assisted Knoevenagel reaction of **2** with diethyl malonate yielded target compound **3** (in 47% for **3a** and 61% for **3b** after purification). Generally, depending on the alkyl-substituent, **3** is well soluble in common organic solvents such as dichloromethane (DCM), tetrahydrofuran (THF) and toluene. The structures of **2** and **3** were proven with the help of high-resolution mass spectrometry and nuclear magnetic resonance (NMR) spectroscopy. These results are presented in the ESI.†

Single-crystals of **3a** were grown from a chloroform-methanol mixture *via* slow evaporation of the solvents. Not surprisingly, **3b** failed to yield crystals suitable for X-ray analysis due to the long and flexible alkyl substituents. In the crystal (Fig. 1), the molecules of **3a** are arranged in a brick-wall fashion with  $\pi$ - $\pi$  distances between neighbouring molecules of 11.4 Å and 12.0 Å, respectively. The dihedral angle between the heterocoronene core (highlighted in blue) and the *N*-alkylphenyl substituent

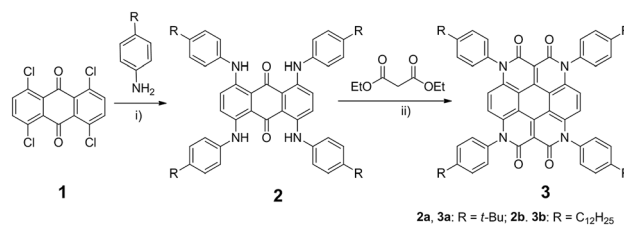
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† Electronic supplementary information (ESI) available: Synthesis and characterization section, TGA and DSC curves of **3**, fluorescence quantum yield measurement for **3a** and perylenetetracarboxydiimide (PDI), and single crystal data for **3a**. CCDC 1581941. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7tc05073a



**Scheme 1** Synthesis of **3**: (i) Pd<sub>2</sub>(dba)<sub>3</sub>, BINAP, Cs<sub>2</sub>CO<sub>3</sub>, toluene, 105 °C, 24 h, **2a**: 58%, **2b**: 44%; (ii) CH<sub>3</sub>COOK, DMF, microwave, 170 °C, 30 min, for **3a**: 47%, **3b**: 61%.



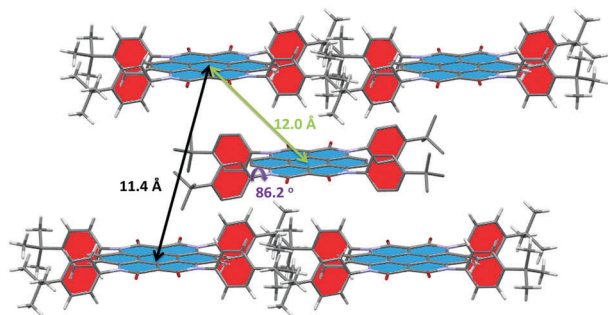


Fig. 1 The single-crystal X-ray determination of **3a**.

(highlighted in red) is  $86^\circ$ , which obviously hinders the  $\pi$ - $\pi$  overlap between the heterocoronene cores. The four adjacent phenyl moieties of **3a** create empty space around the heterocoronene core. This allows the alkylphenyl substituents from neighbouring molecules to penetrate into the resulting voids. The torsion of the phenyl rings is not in the same direction, *i.e.* clockwise or counterclockwise, which is not favourable for molecular self-assembly *via* helical packing with regular intermolecular torsion angles (the random twisting of the alkylphenyls prevents the close packing of heterocoronene cores with consistent angle of rotation).

The optical and electrochemical properties of **3** are presented in Fig. 2. **3a** and **3b** reveal almost identical absorption spectra containing three bands ( $\alpha$ ,  $\beta$ , p) with peaks at maxima of 282 nm ( $\beta$  band), 391 nm (p band) and 540 nm ( $\alpha$  band), with an absorption onset at 570 nm. The emission spectra contain two sub-peaks at 554 and 584 nm, respectively, which reflect a mirror relationship with the  $\alpha$  band of the absorption with Stokes shifts of 14 nm (540–554 nm). The fluorescence of **3** in DCM solution is very weak with fluorescence quantum yields ( $\Phi_f$ ) of  $\sim 2\%$  and fluorescence lifetime of 0.56 ns. Under the same conditions, perylene orange, *i.e.* *N,N'*-bis(2,6-diisopropylphenyl)perylene-tetracarboxydiimide (PDI), presents a  $\Phi_f$  of 98% and fluorescence lifetime of 4.1 ns (data given in ESI†). Unlike most of perylene dyes which have no fluorescence in solid-state, the powders of **3a**, however, show red fluorescence with emission maximum at 610 nm (see ESI†). In this regard, **3** can be considered as a member of aggregation-induced emissive (AIE) materials.<sup>14</sup> Similar to tetraphenylethene (TPE), the central heterocoronene stator of the **3a** molecule is surrounded by four phenyl ring-rotors, which dynamically rotate and scatter the

exciton energy non-radiatively. Therefore, the photoluminescence of **3** is very weak in solution but not in solid. The HOMO and LUMO energy levels of **3** were estimated by cyclic voltammetry in DCM solution (Fig. 2). The (identical) oxidation and reduction onsets of **3a** and **3b** vs. ferrocene/ferrocene<sup>+</sup> ( $\text{Fc}^+/\text{Fc}$ ) are 1.04 V and  $-1.19$  V, respectively. The HOMO and LUMO values were thus calculated as  $-5.8$  eV and  $-3.6$  eV, respectively (Table 1). Compared with PDI, heterocoronene **3** is more easily oxidized owing to its higher HOMO ( $-6.1$  eV for PDI).<sup>15</sup> Additionally, the LUMO energy of **3** is more positive than those of the fullerene PC<sub>71</sub>BM ( $-4.00$  eV)<sup>16a</sup> and PDI ( $-3.8$  eV).<sup>15</sup> When used as acceptor in solar cells, **3** is supposed to furnish a larger gap between HOMO (donor) and LUMO (acceptor), thereby possibly increasing the  $V_{oc}$  value that depends on the energy gap between the HOMO level of the donor and the LUMO level of the acceptor of organic photovoltaics.<sup>16</sup>

The thermal stability of **3** was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (TAG and DSC results shown in ESI†). **3a** and **3b** demonstrate the 5% weight loss at 433 and 515 °C, respectively. The *t*-butyl groups appear to be more stable than the respective *n*-dodecyl groups. Furthermore, the weight loss can be attributed to the decomposition of the alkyl substituents, demonstrating an even higher thermal stability of the aromatic core. The DSC curve of **3a** displays a small endothermic peak at 294 °C, whereas **3b** exhibits a strong endothermic peak at 90 °C. The lower endothermic peak in **3b** can be ascribed to the dodecyl-substituents, which bring about a lower melting point.

A comparison of frontier orbitals of **2**, **3**, coronene (**4**), and 1,4,7,10-tetraazacoronene (**5**)<sup>17</sup> is depicted in Fig. 3. Obviously, **3**, **4**, and **5** possess similar molecular orbitals, but not **2**.

Table 1 The energy levels of **3a** and **3b**

$\lambda_{\text{max}}$ (nm)	Experimental			DFT calculation <sup>b</sup>		
	$E_g^a$	HOMO <sup>b</sup>	LUMO <sup>c</sup>	$E_g^d$	HOMO	LUMO
<b>3a</b> 282; 391; 540	2.18	$-5.84$	$-3.61$	2.23	$-5.82$	$-3.08$
<b>3b</b> 282; 391; 540	2.18	$-5.84$	$-3.61$	2.23	$-5.82$	$-3.08$

<sup>a</sup>  $E_g = 1240/\lambda_{\text{onset}}$ . <sup>b</sup> Estimated vs. vacuum level from  $E_{\text{HOMO}} = -4.80$  eV  $- E_{\text{ox}}$ .

<sup>c</sup> Estimated vs. vacuum level from  $E_{\text{LUMO}} = -4.80$  eV  $- E_{\text{red}}$ .

<sup>d</sup>  $E_g = E_{\text{LUMO}}^{\text{CV}} - E_{\text{HOMO}}^{\text{CV}}$ . The  $E_{\text{ox}}$  and  $E_{\text{red}}$  are calibrated with  $\text{Fc}/\text{Fc}^+$  as the reference.

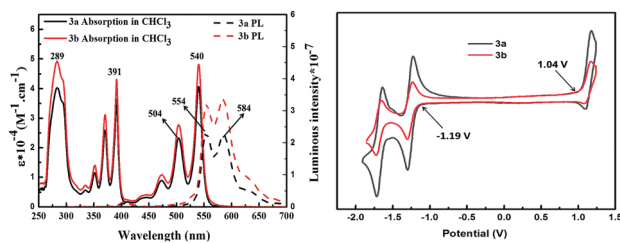


Fig. 2 The absorption and fluorescence spectra of **3a** and **3b** in dilute chloroform solution (left). The CV curves of **3a/b** vs.  $\text{Fc}^+/\text{Fc}$  in DCM solution of  $\text{Bu}_4\text{NPF}_6$  (0.1 M) with a scan rate of  $50$   $\text{mV s}^{-1}$  (right).

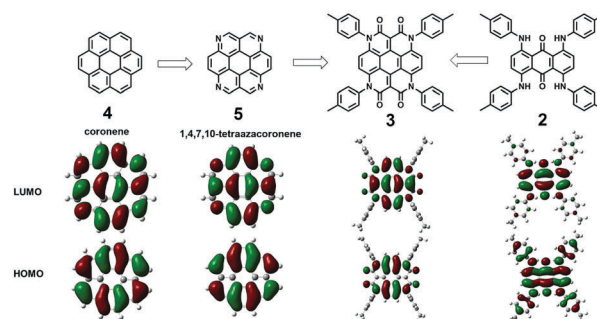


Fig. 3 Representation of the molecular orbitals of **3**, **4** and **5** (DFT calculations at the B3LYP/6-31G(d) level).



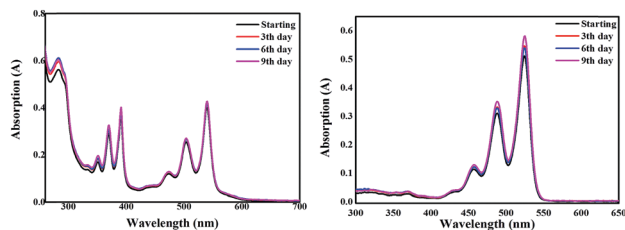


Fig. 4 The photostability (absorption spectra) were recorded after the solution was placed in the open air under sunlight) of **3a** (left) and PDI (right) in DCM solution.

This indicates that the coronene character of **3** is maintained. Compounds **4** and **5** are yellow whereas **3** is dark red. Thus, the four amide groups of **3** lead to a strong change in colour without affecting the molecular orbitals.

The light stability of **3a** was tested by using its DCM solution under sunlight. For comparison, the solution of PDI was prepared at the same concentration. When recording the UV-vis absorption spectra of **3a** and PDI daily (Fig. 4), heterocoronene **3a** shows the same stability as that of PDI. After 9 days of outdoor exposure to sunlight, the absorption spectrum of **3a** remained nearly identical to the initial one. Light fastness is, of course, a key feature of a new chromophore.

## Conclusions

In conclusion, two disc-like heterocoronenes **3a** and **3b** were synthesized from commercially available 1,4,5,8-tetrachloro-9,10-anthraquinone *via* Buchwald-Hartwig coupling and a subsequent Knoevenagel condensation. **3** exhibits similar optical properties to perylenetetracarboxydiimides but shows higher LUMO and HOMO levels than those of PDI. Although **3** has nearly no fluorescence in solution, it reveals a thermal stability up to 515 °C and strong photoluminescence in solid. Additionally, **3** possesses the same photostability as that of PDI dyes, qualifying this new heterocoronene-based chromophore as a promising colorant even for outdoor applications.

## Conflicts of interest

There are no conflicts to declare.

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## References

- (a) S. L. Suraru and F. Würthner, *Angew. Chem., Int. Ed.*, 2014, **53**, 7428; (b) A. Herrmann and K. Müllen, *Chem. Lett.*, 2006, **35**, 978; (c) X. W. Zhan, A. Facchetti, S. Barlow, T. J. Marks, M. A. Ratner, M. R. Wasielewski and S. R. Marder,

- Adv. Mater.*, 2011, **23**, 268; (d) W. Jiang, Y. Li and Z. H. Wang, *Acc. Chem. Res.*, 2014, **47**, 3135.
- C. Sourisseau, *Chem. Rev.*, 2004, **104**, 3851.
- (a) A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra and G. B. Behera, *Chem. Rev.*, 2000, **100**, 1973; (b) A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891; (c) F. Würthner, C. R. Saha-Moller, B. Fimmel, S. Ogi, P. Leowanawat and D. Schmidt, *Chem. Rev.*, 2016, **116**, 962.
- (a) M. Phillips, *Chem. Rev.*, 1929, **6**, 157; (b) K. C. Nicolaou, Y. P. Wang, M. Lu, D. Mandal, M. R. Pattanayak, R. C. Yu, A. A. Shah, J. S. Chen, H. J. Zhang, J. J. Crawford, L. Pasunoori, Y. B. Poudel, N. S. Chowdari, C. Pan, A. Nazeer, S. Gangwar, G. Vite and E. N. Pitsinos, *J. Am. Chem. Soc.*, 2016, **138**, 8235.
- Y. Liu, X. X. Hu, L. L. Wang, X. J. Liu, T. Bing, W. H. Tan and D. H. Shangguan, *Dyes Pigments*, 2017, **145**, 168.
- K. Kotwica, P. Bujak, D. Wamil, M. Materna, L. Skorka, P. A. Gunka, R. Nowakowski, B. Golec, B. Luszczynska, M. Zagorska and A. Pron, *Chem. Commun.*, 2014, **50**, 11543.
- K. Kotwica, P. Bujak, P. Data, W. Krzywiec, D. Wamil, P. A. Gunka, L. Skorka, T. Jaroch, R. Nowakowski, A. Pron and A. Monkman, *Chem. – Eur. J.*, 2016, **22**, 7978.
- R. C. Ahuja, K. Hauffe, R. Schumacher and R. N. Schindler, *Ber. Bunsen Phys. Chem.*, 1982, **86**, 167.
- (a) D. Q. Wu, W. Pisula, M. C. Haberecht, X. L. Feng and K. Müllen, *Org. Lett.*, 2009, **11**, 5686; (b) J. Luo, M. F. Xu, R. Z. Li, K. W. Huang, C. Y. Jiang, Q. B. Qi, W. D. Zeng, J. Zhang, C. Y. Chi, P. Wang and J. S. Wu, *J. Am. Chem. Soc.*, 2014, **136**, 265; (c) Z. B. Zeng, S. Lee, M. Son, K. Fukuda, P. M. Burrezo, X. J. Zhu, Q. B. Qi, R. W. Li, J. T. L. Navarrete, J. Ding, J. Casado, M. Nakano, D. Kim and J. S. Wu, *J. Am. Chem. Soc.*, 2015, **137**, 8572; (d) J. Li, S. Chen, Z. Wang and Q. Zhang, *Chem. Rec.*, 2016, **16**, 1518; (e) J. Li and Q. Zhang, *Synlett*, 2013, 686; (f) J. Li and Q. Zhang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 28049.
- (a) P. E. Hartnett, C. M. Mauck, M. A. Harris, R. M. Young, Y. L. Wu, T. J. Marks and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2017, **139**, 749; (b) R. J. Lindquist, K. M. Lefler, K. E. Brown, S. M. Dyar, E. A. Margulies, R. M. Young and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2014, **136**, 14912; (c) S. T. J. Ryan, R. M. Young, J. J. Henkelis, N. Hafezi, N. A. Vermeulen, A. Hennig, E. J. Dale, Y. L. Wu, M. D. Krzyaniak, A. Fox, W. M. Nau, M. R. Wasielewski, J. F. Stoddart and O. A. Scherman, *J. Am. Chem. Soc.*, 2015, **137**, 15299.
- (a) H. L. Dong, X. L. Fu, J. Liu, Z. R. Wang and W. P. Hu, *Adv. Mater.*, 2013, **25**, 6158; (b) L. Flamigni, B. Ventura, M. Tasior, T. Becherer, H. Langhals and D. T. Gryko, *Chem. – Eur. J.*, 2008, **14**, 169; (c) H. Langhals, *Helv. Chim. Acta*, 2005, **88**, 1309–1343; (d) Y. Zagranyski, L. Chen, D. Jansch, T. Gessner, C. Li and K. Müllen, *Org. Lett.*, 2014, **16**, 2814; (e) G. Li, Y. Zhao, J. Li, J. Cao, J. Zhu, X. W. Sun and Q. Zhang, *J. Org. Chem.*, 2015, **80**, 196.
- (a) R. Rieger, M. Kastler, V. Enkelmann and K. Müllen, *Chem. – Eur. J.*, 2008, **14**, 6322; (b) C. L. Eversloh, C. Li and K. Müllen, *Org. Lett.*, 2011, **13**, 4148; (c) Q. Zhang,



- H. Q. Peng, G. S. Zhang, Q. Q. Lu, J. Chang, Y. Y. Dong, X. Y. Shi and J. F. Wei, *J. Am. Chem. Soc.*, 2014, **136**, 5057; (d) Q. Yan, K. Cai, C. Zhang and D. Zhao, *Org. Lett.*, 2012, **14**, 4654; (e) W. Mao, J. Zhang, X. Li, C. Li and H. Tian, *Chem. Commun.*, 2017, **53**, 5052; (f) G. Li, W.-W. Xiong, P.-Y. Gu, J. Cao, J. Zhu, R. Ganguly, Y. Li, A. C. Grimsdale and Q. Zhang, *Org. Lett.*, 2015, **17**, 560.
- 13 S. Hahn, F. L. Geyer, S. Koser, O. Tverskoy, F. Rominger and U. H. F. Bunz, *J. Org. Chem.*, 2016, **81**, 8485.
- 14 J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam and B. Z. Tang, *Chem. Rev.*, 2015, **115**, 11718.
- 15 S. K. Lee, Y. B. Zu, A. Herrmann, Y. Geerts, K. Müllen and A. J. Bard, *J. Am. Chem. Soc.*, 1999, **121**, 3513.
- 16 (a) W. C. Tsoi, D. T. James, J. S. Kim, P. G. Nicholson, C. E. Murphy, D. D. C. Bradley, J. Nelson and J. S. Kim, *J. Am. Chem. Soc.*, 2011, **133**, 9834; (b) D. Sun, D. Meng, Y. H. Cai, B. B. Fan, Y. Li, W. Jiang, L. J. Huo, Y. M. Sun and Z. H. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 11156; (c) D. Meng, D. Sun, C. M. Zhong, T. Liu, B. B. Fan, L. J. Huo, Y. Li, W. S. Jiang, H. S. Choi, T. Kim, J. Y. Kim, Y. M. Sun, Z. H. Wang and A. J. Heeger, *J. Am. Chem. Soc.*, 2016, **138**, 375; (d) S. S. Chen, Y. H. Liu, L. Zhang, P. C. Y. Chow, Z. Wang, G. Y. Zhang, W. Ma and H. Yan, *J. Am. Chem. Soc.*, 2017, **139**, 6298; (e) Y. Zhong, M. T. Trinh, R. S. Chen, W. Wang, P. P. Khlyabich, B. Kumar, Q. Z. Xu, C. Y. Nam, M. Y. Sfeir, C. Black, M. L. Steigerwald, Y. L. Loo, S. X. Xiao, F. Ng, X. Y. Zhu and C. Nuckolls, *J. Am. Chem. Soc.*, 2014, **136**, 15215.
- 17 (a) M. Takase, T. Narita, W. Fujita, M. S. Asano, T. Nishinaga, H. Benten, K. Yoza and K. Müllen, *J. Am. Chem. Soc.*, 2013, **135**, 8031; (b) S. A. Tucker, W. E. Acree, M. J. Tanga, M. Zander, J. C. Fetzer, S. Tokita, K. Hiruta, K. Kitahara and H. Nishi, *Appl. Spectrosc.*, 1991, **45**, 1188.

