From anthraquinone to heterocoronene as stable red chromophore†

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Herein we combine coronene12 (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)15 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 ESL†.

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 π–π 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...
(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 of $2\%$ and fluorescence lifetime of 0.56 ns. Under the same conditions, perylene orange, $3a$, 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 $2$, $3$, corocene ($4$), and 1,4,7,10-tetrazacoronene ($5$) is depicted in Fig. 3. Obviously, $3$, $4$, and $5$ possess similar molecular orbitals, but not $2$.

| $\lambda_{\text{max}}$ (nm) | Experimental $E_g$ | HOMO | LUMO | DFT calculation $E_g$ | HOMO | LUMO |
|--------------------------|------------------|------|------|----------------------|------|------|
| $3a$ | 282; 391; 540 | 2.18 | $-5.84$ | $-3.61$ | 2.23 | $-5.82$ | $-3.08$ |
| $3b$ | 282; 391; 540 | 2.18 | $-5.84$ | $-3.61$ | 2.23 | $-5.82$ | $-3.08$ |

$^a$ $E_g = 1240/\lambda_{\text{max}}$; $^b$ Estimated vs. vacuum level from $E_{\text{HOMO}} = -4.80$ eV $- E_{\text{vac}}$; $^c$ Estimated vs. vacuum level from $E_{\text{LUMO}} = -4.80$ eV $- E_{\text{vac}}$; $^d$ $E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$. The $E_{\text{vac}}$ and $E_{\text{vac}}$ are calibrated with Fe/Fe$^{3+}$ as the reference.

![Fig. 2](https://example.com) The absorption and fluorescence spectra of $3a$ and $3b$ in dilute chloroform solution (left). The CV curves of $3a/b$ vs. Fe$^{3+}$/Fe$^{2+}$ in DCM solution of Bu$_4$NPF$_6$ (0.1 M) with a scan rate of 50 mV s$^{-1}$ (right).

![Fig. 3](https://example.com) Representation of the molecular orbitals of $3$, $4$ and $5$ (DFT calculations at the B3LYP/6-31G(d) level).
LUMO and HOMO levels than those of PDI. Although properties to perylenetetracaboxdiimides but shows higher
3
9,10-anthraquinone
3a

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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 heterocorones 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 perylene-tetracarbonitrides 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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