

Synthesis, Characterization, and Self-Assembly of Nitrogen-Containing Heterocoronenetetracarboxylic Acid Diimide Analogues: Photocyclization of N-Heterocycle-Substituted Perylene Bisimides

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Abstract: Novel dibenzocoronenetetracarboxylic acid diimide analogues and naphthoperylenetetracarboxylic acid diimide analogues containing imidazole, 1,2,4-triazole, and pyrazole rings embedded as functional constituents within the parent hydrocarbon backbone have been synthesized. The π -rich and π -poor heterocycles have dif-

ferent influences on the physical properties of the parent benzocoronene-tetracarboxylic acid diimide and naphthoperylenetetracarboxylic acid di-

imide systems. The π -rich **3** was able to self-assemble into one-dimensional nanostructures through strong π - π stacking, whereas the π -poor **8** lacked the one-dimensional self-assembly capability, thus offering the potential to control the self-assembly capability of the π -conjugated perylene core by decoration with N-heterocycles.

Keywords: heterocycles • nanostructures • perylene • photocyclization • self-assembly

Introduction

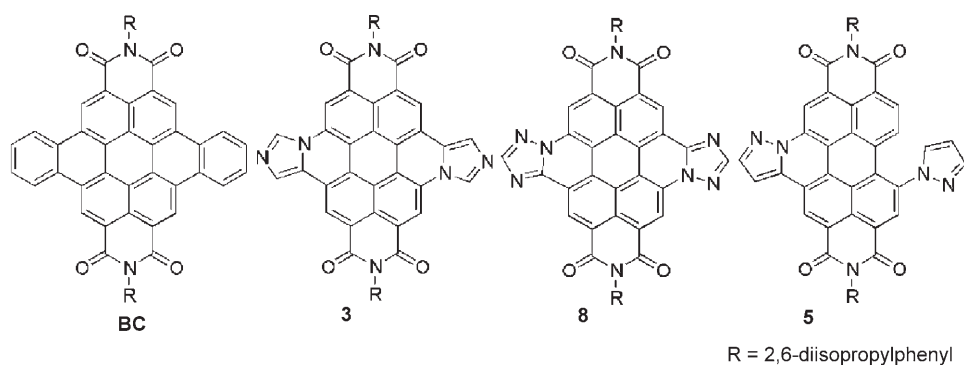
Red chromophores based on perylenetetracarboxylic acid diimide systems have recently attracted considerable investigator attention and have been shown to be suitable in various applications, such as fluorescent solar collectors,^[1] photovoltaic devices,^[2] dye lasers,^[3] molecular switches,^[4] and light-emitting diodes,^[5] thanks to their exclusive chemical, thermal, and photochemical stability and their ability to self-assemble into extended structures.^[6] They were seen to be highly absorbing in the visible to near-IR region ($\epsilon \approx 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) and to emit fluorescence with quantum yields near unity;^[7] the interest in these compounds being largely due to these high fluorescence quantum yields and their tunable absorption and emission properties. The exten-

sion of the aromatic core of perylene is a currently active topic in chemistry,^[8] the goal being to extend the range of application of these chromophores as functional dyes to improve their performance in devices. Perylenetetracarboxylic acid diimides have been functionalized in one bay region through the use of Diels–Alder reactions followed by reduction or mononitration and cyclization,^[8b] or through enlargement of the aromatic π system by palladium-catalyzed ring annulation.^[8c] We have previously developed a phototriggered intramolecular cyclization of 1,7-diphenylperylene diimide systems to produce core-extended perylene chromophores—dibenzocoronenetetracarboxylic acid diimide analogues (**BC**)—whilst the anellation of perylene-3,4-dicarboxylic acid imide with heterocycles has also been reported.^[9] The physical behavior of π -conjugated materials could be dramatically modulated through the incorporation of electron-rich or electron-deficient arenes directly into their conjugated backbones. Some recent works have established self-assembly through strong π - π stacking as an effective approach to one-dimensional nanostructures based on aromatic organic molecules,^[10] particularly in larger macrocyclic aromatic molecules such as hexabenzocoronene.^[11] However, the substitution of perylene-3,4:9,10-tetracarboxylic acid diimides (PTIs) with π -rich or π -poor heterocycles as donor or acceptor moieties has not previously been reported. Imidazoles have been observed to act as good ligands to transition-metal ions for forming coordinating complexes^[12] and

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the most widely used motif for electron-transport/hole-blocking functionality is based on the incorporation of electron affinity-enhancing, nitrogen-containing five-membered heteroaromatic rings;^[13] 1,2,4-triazole was used to enhance the electron affinity of electron-transport materials,^[14] whereas pyrazole has been used to achieve blue light-emitting diodes.^[15]

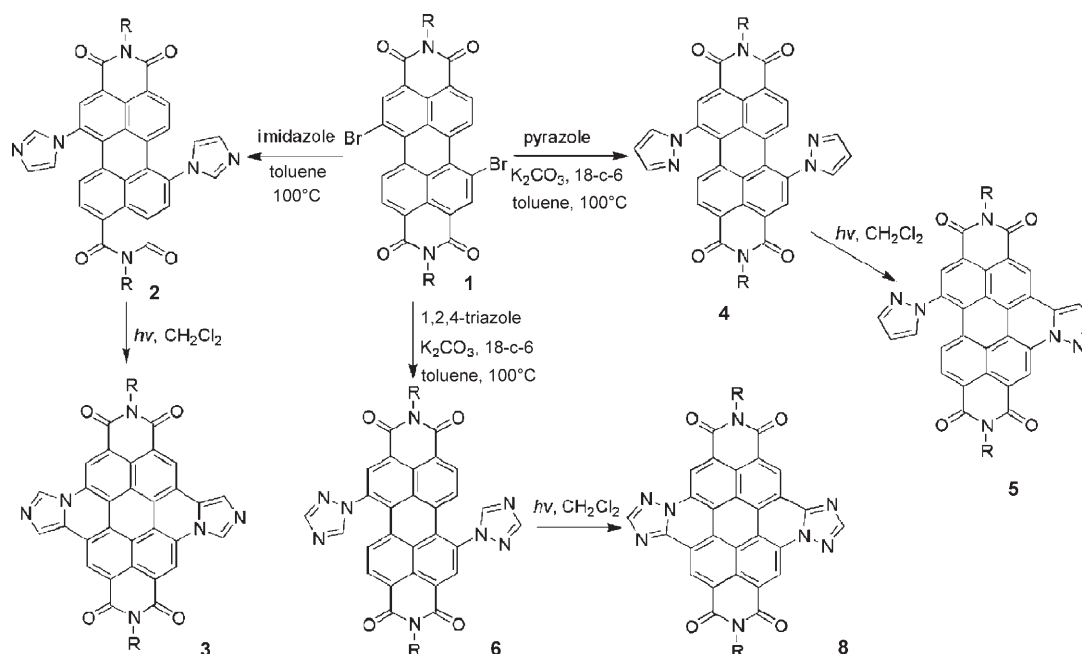
When coronene derivatives were further functionalized with carboximide groups, electron-poor aromatic systems were obtained, to provide electron-transporting n-type materials.^[16] Apart from electron-withdrawing peripheral substituents, introduction of nitrogen in the core could also reduce the electron density of the aromatic system. Different azaaromatic compounds of varying size, the smallest being pyridine and triazine units, were found to give rise to columnar mesophases with different degrees of order,^[17] whereas extended electron-deficient disks based on hexaazatriphenylene^[18] and quinoxaline^[19] cores had charge-carrier mobility of up to $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}$.^[19b]

Here we report a variety of PTIs substituted with N-heterocycles, together with the synthesis of novel heterocycle-embedded benzocorononetetracarboxylic acid diimide analogues and naphthoperylene-tetracarboxylic acid diimide analogues through the enlargement of the aromatic π systems of available perylene derivatives by photocyclization. These N-heterocycles and the ligand properties of imidazole offered us the potential to tune the electron-transporting properties of PTIs for effective fabrication of devices and easy production of organic-inorganic hybrid materials. Self-organization of nitrogen heterocorononetetracarboxylic acid diimide systems may enable the creation of unique aggregate structures as a result of the stacking of the central perylene rings. We have detailed the self-assembly behavior of the N-heterocycles and have established by scanning electron micrograph (SEM) observation that heterocycle-embedded benzocorononetetracarboxylic acid diimide systems are able to form different nanostructures in different solvents.

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Results and Discussion

The substitution of 1,7-dibromoperylene-tetracarboxylic acid diimide^[20,21] with imidazole, 1,2,4-triazole, and pyrazole moieties, connected through their imino N-H groups, afforded **2**, **4**, and **6** by the S_NAr amination mechanism (Scheme 1).^[22]



Scheme 1. Synthesis of the N-heterocycle-substituted perylene diimides and their photocyclization (R = 2,6-diisopropylphenyl; 18-c-6 = [18]crown-6).

Compound **2** was obtained in high yield (84%) through direct heating of a mixture of imidazole and 1,7-dibromoperylenetetracarboxylic acid diimide in toluene, but the reactions of 1,2,4-triazole and pyrazole with 1,7-dibromoperylenetetracarboxylic acid diimide had to be in the presence of K_2CO_3 and [18]crown-6. In these N-heterocycle-substituted PTIs, the orientations of the N-heterocycles were restricted to perpendicular to the perylene units as observed by means of NMR analysis (the unsubstituted protons in the perylene bay region were shifted upfield by the N-heterocycles). The reaction between imidazole and the diimide afforded a mixture of **2** and the monocyclized species, whereas irradiation of **2** produced the doubly cyclized **3**.

Substitution of the 1-bromoperylene diimide **9** with imidazole, through the imino N–H group, directly afforded monocyclized **10** without the intermediate (Scheme 2). Analysis of the monocyclized product by high-resolution fast-atom bombardment (HRFAB) mass spectrometry indicated the expected mass ion with loss of two hydrogen atoms. The side of the plane at which the imidazole ring had been bonded was clearly shown by four singlets at $\delta = 10.32, 9.54, 8.78,$ and 8.21 ppm. The 1H NMR spectra of the doubly cyclized **3** (Scheme 1) were characterized by four singlets (each representing two hydrogens) at $\delta = 10.47, 9.80, 8.93,$ and 8.26 ppm.

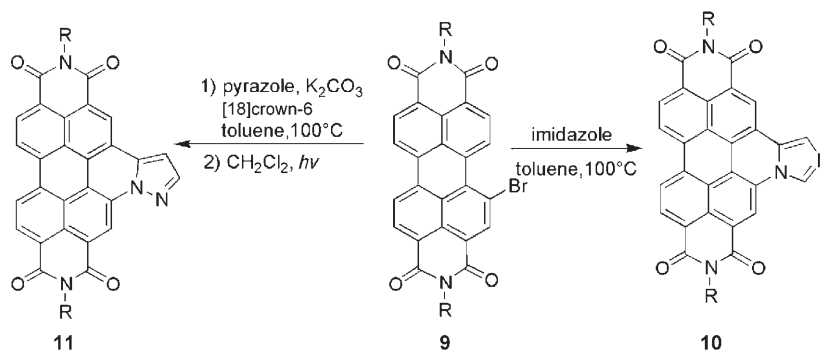
The triazole and pyrazole groups could also be cyclized onto the perylene main core, though at relatively slow rates (in the case of triazole, monocyclized **7** and doubly cyclized **8** were obtained, whereas in that of pyrazole only monocyclized product was separated).

All of these compounds were highly soluble in various organic solvents, such as CH_2Cl_2 , $CHCl_3$, toluene, and acetone, except in the case of the cyclized product **3**, which only dissolved readily in CH_3CN , pyridine, and DMSO.

Room-temperature absorption and emission spectra of these compounds are shown in Figure 1 and their photophysical properties are summarized in Table 1. Compounds **2**, **4**, and **6** showed the characteristic vibronic fine structure of the perylene core $\pi-\pi^*$ transition. Because of the steric constraints, the orientations of the imidazole, triazole, and pyrazole moieties were restricted to orthogonal to the perylene ring, so the π -conjugative interactions were minimal, as a consequence of which the λ_{max} value for **2** was only slightly redshifted (by 8 nm) relative to that for the dibromoperylenetetracarboxylic acid diimide **1** (527 nm).^[21] The λ_{max} of **4** was redshifted by 12 nm to 539 nm, due to the electron-donor properties of the pyrazole unit, whilst the λ_{max} of **6** was blueshifted by 3 nm to 524 nm, due to the electron affinity of the triazole moiety. These N-heterocycle-substituted derivatives all fluoresced with quantum yields $\Phi_f > 0.3$, as

determined relative to **1** ($\Phi_f = 0.76$),^[21] although the Stokes shifts of **2** (55 nm) and **4** (47 nm) were greater than that of **6** (35 nm).

After cyclization, **3** showed a sharp band with a defined structure at $\lambda = 351$ nm, the typical perylene vibronic structure had disappeared, and four bands at $\lambda = 453, 468, 517,$ and 558 nm were observed in the longer-wavelength region. A similar phenomenon was observed in the case of **11**, whereas **8** showed the typical absorption structure of dibenzocorononetetracarboxylic acid diimide analogues (that is, a set of bands with defined structures between $\lambda = 289-337$ nm



Scheme 2. Synthesis of heterocycle-embedded naphthoperylenetetracarboxylic acid diimides **10** and **11** (R = 2,6-diisopropylphenyl).

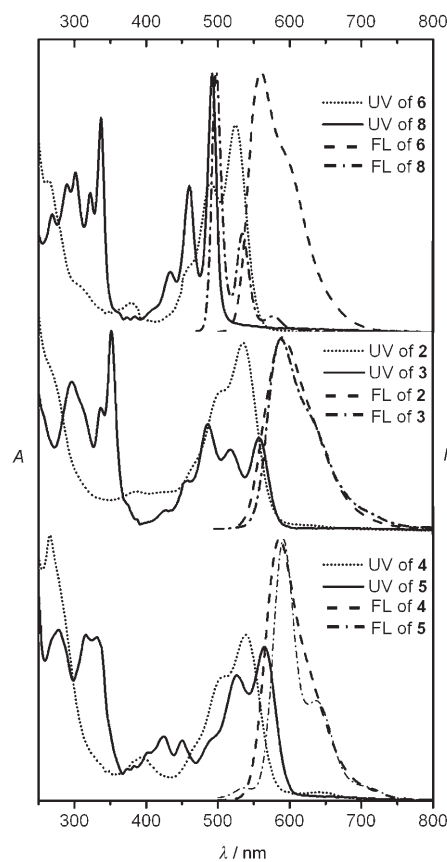


Figure 1. Absorption and emission spectra of the photocyclized N-heterocycle-substituted perylenes and their precursors.

Table 1. Photophysical and electrochemical properties of the photocyclized heterocycle-substituted perylenes and their precursors.

| | Abs ^[a] λ_{\max} [nm] | PL ^[b] λ_{\max} [nm] | $\Phi_{\text{fl}}^{\text{[c]}}$ [%] | $E_{1/2, \text{ox}}$ [V vs Fc/Fc ⁺] ^[e] | $E_{1/2, \text{red}}$ [V vs Fc/Fc ⁺] ^[e] | HOMO/LUMO [eV] ^[f] |
|-----------|---|--|--|---|--|----------------------------------|
| 1 | 527 | 547 | 76 | 1.50 | -0.67, -0.89 | -6.30/-4.13 |
| 2 | 535 | 590 | 33 | 1.40 | -0.65, -0.89 | -6.20/-4.15 |
| 3 | 558, 468, 351 | 587 | 49 | 1.32 | -0.78, -0.94, -1.07 | -6.12/-4.02 |
| 10 | 554, 511, 485, 350 | 575 | 43 | 1.29 | -0.76, -0.87, -1.04 | -6.09/-4.04 |
| 6 | 524 | 559 | 69 | 1.53 | -0.56, -0.81 | -6.33/-4.24 |
| 7 | 505, 315 | 522 | 70 ^[d] | 1.62 | -0.53, -0.64, -0.89 | -6.42/-4.27 |
| 8 | 492, 460, 433, 337, 332, | 498 | 74 ^[d] | 1.49 | -0.56, -0.74, -1.01 | -6.29/-4.24 |
| 4 | 539, 504, 391 | 586 | 54 | 1.55, 1.25 | -0.65, -0.89 | -6.05/-4.15 |
| 5 | 565, 526, 450, 424, 316 | 591 | 41 | 1.59, 1.36 | -0.67, -0.77, -0.95 | -6.16/-4.13 |
| 11 | 560, 524, 445, 418, 397, 316 | 583 | 50 | 1.45, 1.32 | -0.71, -0.84, -1.00 | -6.12/-4.09 |

[a] In CHCl₃. [b] In CHCl₃, upon excitation at the absorption maximum. [c] In CHCl₃, *N,N'*-bis(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid diimide ($\Phi_{\text{fl}}=0.76$ in CHCl₃^[21]) as the standard. [d] In CHCl₃, dibenzocoronenetetracarboxylic acid diimide ($\Phi_{\text{fl}}=0.80$ in CHCl₃^[8c]) as the standard. [e] In CH₃CN containing 0.05 M *n*Bu₄NPF₆ as a supporting electrolyte. [f] HOMO and LUMO levels with respect to zero vacuum level were estimated directly from CV data.

and the typical perylene vibronic structure with a maximum absorption band at $\lambda=492$ nm, hypsochromically shifted by 32 nm). Compound **8** emitted an intensive green-yellow fluorescence with a maximum (in CHCl₃) at 498 nm, hypsochromically shifted by about 61 nm in relation to **6** (559 nm). In the case of the imidazole-substituted perylene, the cyclization had a negligible influence on the emission maxima. More interestingly, in the monocyclized product obtained from the pyrazole-substituted perylene, the λ_{\max} was redshifted, and a set of new bands (360–460 nm) had appeared in the trough region of the original perylene or dibenzocoronene analogues, so the absorption bands of the cyclized pyrazole-substituted perylene system spanned a wide range of the UV and visible spectrum, from 300 to 600 nm, making it an ideal system for harvesting polychromatic light. The emission of **5** was only slightly redshifted.

Cyclic voltammetry (CV) was used to examine the electrochemical behavior of N-heterocycle-substituted perylenes and their photocyclized analogues (Figure 2; Table 1). Compounds **2** and **6** each exhibited one irreversible oxidation potential, at 1.40 and 1.53 V, respectively, whereas **4** exhibited

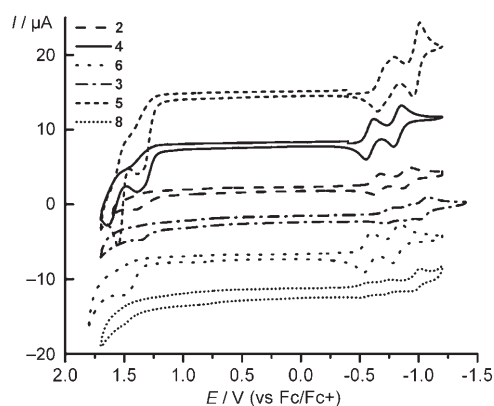


Figure 2. Cyclic voltammograms of the photocyclized heterocycle-substituted perylenes and their precursors.

two irreversible oxidation potentials, at 1.25 and 1.55 V. The oxidation potentials of **2** and **4** were lower than those of 1,7-dibromo-*N,N'*-bis(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxylic acid diimide (**1**), which clearly indicated the significant HOMO-raising effect of using π -electron-rich imidazole and pyrazole units as constitutional moieties. The oxidation potential of **6**, however, was a little higher than that of **1**, which may be due to the π -electron-deficient 1,2,4-triazole moiety rendering oxidation more difficult. The N-heterocycle-substituted perylene deriva-

tives all showed two reversible, well separated, one-electron reduction waves, with the imidazole and pyrazole moieties only inducing positive shifts of 20 mV. Compound **6** showed a larger positive shift in its redox potential (110 mV).

After cyclization there were two one-electron waves and one two-electron reduction wave (Figure 2), and the first reduction potential of **3** was negatively shifted by about 130 mV. The first reduction potential of **8** was unchanged, whereas that of **5** was negatively shifted a little (20 mV). The oxidation process was irreversible, similarly to the cases of irreversible oxidation observed for other azaaromatic conjugated systems and attributable to oxidation processes involving the nitrogen lone pairs.^[23] There was a tendency of the imidazole- and pyrazole-substituted perylenes (cyclized or not) to be more easily oxidized, whereas the triazole-substituted perylene (and the cyclized product) were more difficult.

Table 1 also lists the HOMO and LUMO energy levels of these compounds, taken directly from the cyclic voltammograms. The electronic structure of the parent perylene-3,4:9,10-tetracarboxylic acid diimide was perturbed significantly after its substitution with N-heterocycles. Substitution of the backbone with electron-rich heterocycles such as imidazole and pyrazole effectively extended the π -conjugation, raising the HOMO level and lowering the LUMO level, resulting in a smaller energy gap. Upon embedding of electron-deficient 1,2,4-triazole as a constituent moiety, this modification resulted in shifts of both the HOMO and LUMO levels to lower levels. Upon cyclization, the HOMO and LUMO levels of cyclized compounds tended to be raised.

Upon cyclization, the compounds' coordination abilities disappeared, due to the dispersion of the nitrogen lone pairs over the whole aromatic plane, but with the increase in the size of the core aromatic system, the π - π stacking of the perylene backbones was enhanced. Lengthy π -conjugated oligomers have been utilized as building blocks for the formation of well-defined supramolecular structures,^[24] organi-

zation of π -conjugated oligomers having been achieved by utilization of thermotropic and lyotropic liquid crystallinity, self-assembly of block copolymers, and complexation through noncovalent bonds such as hydrogen bonds.^[25] Organizational control over the orientation of π -conjugated oligomers is important for the development of nanoscopic molecular systems.

It was speculated that the combination of a π -rich N-heterocycle with a π -conjugated perylene core might give rise to unique aggregation behavior because of their intermolecular π - π interactions, and this was confirmed by ¹H NMR and SEM studies as shown below. Compound **3** is also an amphiphile, as the imidazole units exhibit hydrophilic properties and the perylene core shows hydrophobic interactions in specific solvent environments.^[26]

¹H NMR spectra of **3** were measured in CDCl₃ and [D₆]DMSO, and their expanded aromatic regions are shown in Figure 3. In CDCl₃, peaks at δ =10.47 and 9.80 ppm were assigned to the perylene protons (A and B), and peaks at

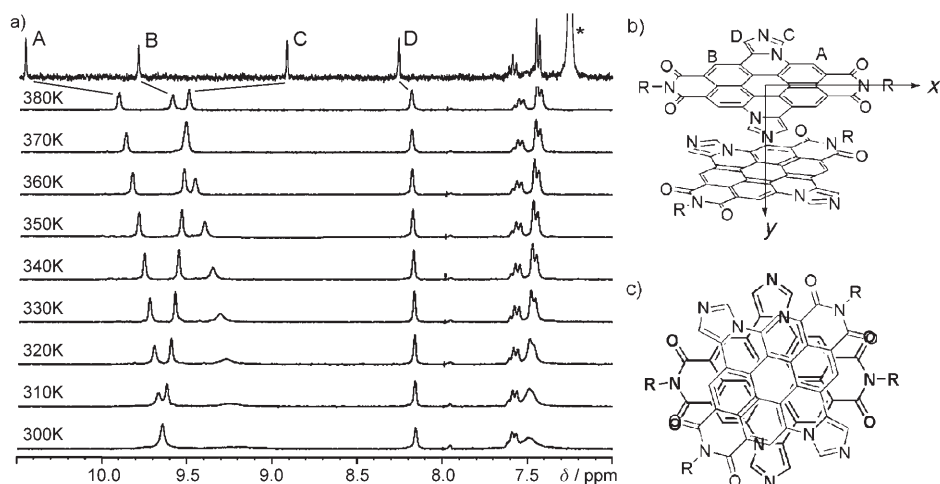


Figure 3. a) ¹H NMR spectrum (400 MHz) of **3** in CDCl₃ (top), and temperature-dependent ¹H NMR spectra of **3** recorded at 300 MHz in [D₆]DMSO. Side view (b) and top view (c) models for the aggregation behavior of **3**.

δ =8.93 and 8.26 ppm were assigned to the cyclized imidazole protons (C and D). In [D₆]DMSO at room temperature, there were two sharp peaks at 8.15 and 9.64 ppm and one broad peak at δ =9.0–9.4 ppm, whereas the peak for the protons at the 3,5-positions in the 2,6-diisopropylphenyl moiety was also broadened. This room-temperature NMR spectrum implied dynamic processes on the NMR timescale, so variable-temperature NMR spectra of **3** were recorded in [D₆]DMSO, allowing for a wide temperature window (Figure 3). As the temperature was increased, the broad peak at δ =9.0–9.4 ppm became sharp and was shifted to 9.58 ppm, the peak at 9.64 ppm was split into two peaks, one shifted to 9.89 ppm and the other to 9.48 ppm, the peak at 8.15 ppm experienced no changes, and the broad peak for the protons at the 3,5-position in the 2,6-diisopropylphenyl moiety became sharp. The peaks displaying evident down-

field shift effects with increasing temperature were assigned to the perylene protons (A and B), as indicated in Figure 3. From the above results, we were able to infer that **3** can self-assemble in polar solvents through π - π interactions, forming rodlike oligomers, and that additional solvophobic forces can further strengthen attractive intermolecular stacking. We were also able to propose a model for the aggregate behavior of **3** (Figure 3b,c). Because of the steric hindrance between 2,6-diisopropylphenyl groups in the case of parallel stacking and the steric hindrance between 2,6-diisopropylphenyl group and imidazole in the case of cross-stacking, the two adjacent molecules are stacked with an angle of aberration of about 45°. Rate constants^[27] (*k*) for **3** were determined by using proton lineshape analysis,^[28] and an Eyring plot^[29] (Figure 4) was constructed to estimate the thermodynamic parameters. The enthalpy of activation (ΔH^\ddagger) was found to be +56.8 kJ mol⁻¹, and the entropy of activation (ΔS^\ddagger) was found to be -61.4 J mol⁻¹ K⁻¹.

The enlarged PTI molecules favored the formation of

nanostructures along one dimension: the red color of a solution of **3** in CH₃CN (10⁻⁴ M) became weak and some precipitates were observed after the system had been kept at room temperature for one week. The precipitates were dispersed in CH₃CN by means of ultrasonification and cast on a silicon slide for SEM measurement, with the obtained SEM images showing well-defined rhombic structures as shown in Figure 5A. Direct casting of the solution of **3** in CH₃CN (5 × 10⁻⁵ M) on the silicon slide resulted in uniform nanofiber structures (Figure 5B). Similar nanofiber structures were also found in

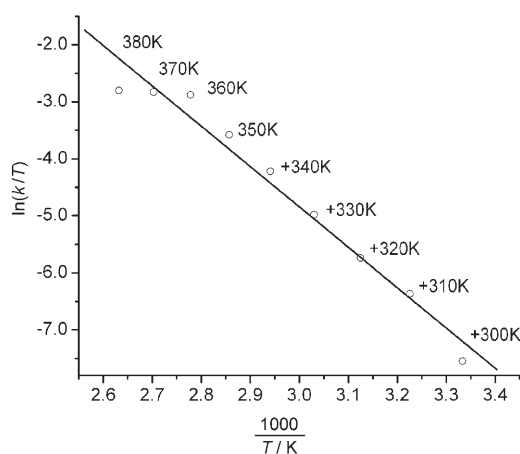


Figure 4. Eyring plot for **3** obtained by proton lineshape analysis.

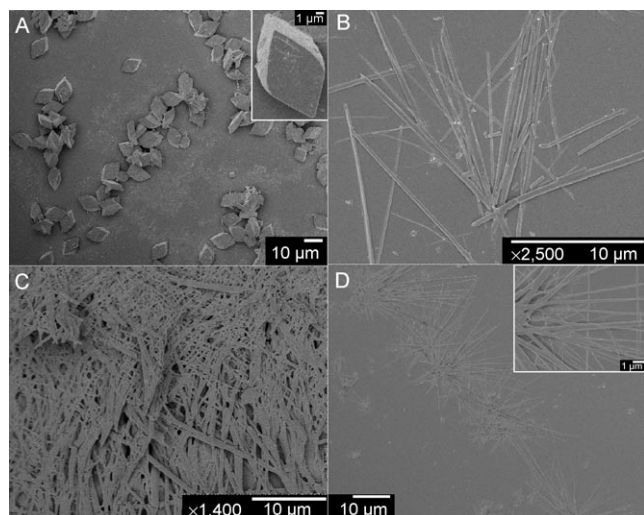


Figure 5. SEM images of **3**: A) rhombic structures precipitated from CH_3CN , together with nanofibers (gold stained) cast from B) CH_3CN , D) pyridine, and C) a nanofiber network from an *n*-hexane/pyridine mixture. The scale bars of the insets in A and D represent 1 μm .

the case of a pyridine solution (Figure 5D), except that the nanofibers tended to grow from some kernels. We also obtained a nanofiber network by using the liquid/liquid diffusion method: *n*-hexane was used to cover the solution of **3** in pyridine, a large quantity of entangled nanofibers being obtained after diffusion for three days (Figure 5C). For comparison, we also recorded images of the electron-deficient 1,2,4-triazole-decorated perylene, for which only irregular structures were found (see the Supporting Information, Figure S3). This lack of one-dimensional self-assembly may be due to the electron-deficiency of the π -conjugated perylene core. We can therefore control the self-assembly capability of the π -conjugated perylene core by decoration with N-heterocycles, and can further control the aggregate structures by tuning the solvents.

Conclusion

In conclusion, we have established efficient syntheses of novel heterocycle-embedded (**3** and **8**) benzocoronenetetracarboxylic acid diimide analogues and naphthoperylenetetracarboxylic acid diimide analogues (**5**, **10**, and **11**). The physical properties of the parent benzocoronenetetracarboxylic acid diimide and naphthoperylenetetracarboxylic acid diimide units were significantly altered through the introduction of π -rich or π -poor heterocycles as constituents. The π -rich **3** was able to self-assemble into one-dimensional nanostructures as a result of strong π - π stacking, while the π -poor **8** lacked the one-dimensional self-assembly capability, which offered us the potential to control the self-assembly capability of the π -conjugated perylene core through decoration with N-heterocycles, and also to control the aggregate structures further by tuning of the solvents.

Experimental Section

Unless stated otherwise, all reagents and anhydrous solvents were purchased from Aldrich Chemicals and were used without further purification. 1-Bromo-*N,N'*-bis(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxylic acid diimide^[32] was prepared as described in the literature. Column chromatography (CC): silica gel (160–200 meshes). TLC glass plates coated with silica (F254) were visualized under UV light. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 instrument, at a constant temperature of 25 °C. Chemical shifts are reported in parts per million from low to high field and are referenced to tetramethylsilane (TMS). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometric measurements were performed on a Bruker Biflex III MALDI-TOF instrument, UV/Vis spectra were measured on a Hitachi U-3010 spectrometer, and FTIR spectra were recorded as KBr pellets on a Perkin-Elmer System 2000 spectrometer. Fluorescence excitation and emission spectra were recorded with a Hitachi F-4500 FL fluorimeter at a constant temperature of 25 °C.

General method for photocyclization: Compounds for cyclization (0.01–0.02 mmol) were dissolved in CH_2Cl_2 (20 mL) in a quartz vessel. The solution was directly irradiated in sunlight, the progress being monitored by TLC. After the photocyclization was complete the reaction mixture was concentrated under reduced pressure to afford the crude product, which was purified by using column chromatography.

Cyclic voltammetry (CV): For this work, CV experiments were performed at a scan rate of 10 mVs^{-1} , with use of a glassy carbon electrode as a working electrode and Ag/AgCl as a reference electrode. CV was performed in CH_3CN with *n* Bu_4NPF_6 (0.05 M) as a supporting electrolyte, in which the ferrocene/ferrocenium ion (Fc/Fc^+) redox couple gives $E_{1/2} = 0.40$ V. The HOMO and LUMO energy levels can be deduced by using the following:^[30] HOMO [eV] = $[-4.8 - (\text{HOMO of ferrocene with respect to the zero vacuum level}^{[31]}) - (E_{1/2} \text{ of the first oxidation potential}) + (0.40)]$; LUMO [eV] = $[-4.8 - (E_{1/2} \text{ of the first reduction potential}) - (0.40)]$.

***N,N'*-Bis(2,6-diisopropylphenyl)-1,7-bis(imidazol-1-yl)perylene-3,4:9,10-tetracarboxylic acid diimide (2):** A mixture of 1,7-dibromo-*N,N'*-bis(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxylic acid diimide (158 mg, 0.2 mmol) and imidazole (136 mg, 2 mmol) in toluene was stirred at 100 °C for 10 h. After cooling to room temperature, the mixture was washed with water, the organic phase was dried with Na_2SO_4 , the solvent was removed by reduced pressure, and the crude product was obtained. Purification was accomplished by using column chromatography on silica gel with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (10:1) to give **2** (141 mg, 84 %). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.71$ (s, 2H), 8.48 (d, $J = 8.1$ Hz, 2H), 7.76 (s, 2H), 7.53–7.49 (m, 4H), 7.35 (d, $J = 7.8$ Hz, 4H), 7.31 (s, 2H), 7.11 (d, $J = 8.1$ Hz, 2H), 2.71 (sept, $J = 6.7$ Hz, 4H), 1.17 ppm (d, $J = 6.7$ Hz, 24H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 162.6$, 162.4, 145.5, 135.7, 134.8, 133.0, 132.9, 132.2, 131.2, 130.0, 129.9, 129.8, 129.4, 128.7, 127.9, 124.4, 124.3, 123.1, 118.3, 29.3, 24.0 ppm; IR (KBr): $\tilde{\nu} = 1709$, 1670, 1596, 1428, 1340, 1249, 1199, 1145, 1032, 909, 733 cm^{-1} ; MS TOF: m/z calcd for $\text{C}_{54}\text{H}_{46}\text{N}_6\text{O}_4$: 842.35; found: 842.3.

***N,N'*-Bis(2,6-diisopropylphenyl)-1,7-bis(triazol-1-yl)perylene-3,4:9,10-tetracarboxylic acid diimide (6):** A mixture of 1,2,4-triazole (138 mg, 2 mmol), anhydrous potassium carbonate (55 mg, 0.4 mmol), and [18]crown-6 (105 mg, 0.4 mmol) was stirred in toluene (50 mL) at room temperature, and 1,7-dibromo-*N,N'*-bis(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxylic acid diimide (158 mg, 0.2 mmol) was added. The reaction mixture was heated at reflux under nitrogen with stirring for 12 h. After the system had cooled to room temperature, the solvent was removed under reduced pressure and the crude product was obtained. Purification was accomplished by using column chromatography on silica gel with CH_2Cl_2 to give **6** (152 mg, 90 %). ^1H NMR (600 MHz, CDCl_3): $\delta = 8.80$ (s, 2H), 8.51 (d, $J = 8.0$ Hz, 2H), 8.50 (s, 2H), 8.41 (s, 2H), 7.52 (t, $J = 8.7$ Hz, 2H), 7.36 (d, $J = 8.8$ Hz, 4H), 7.05 (d, $J = 8.0$ Hz, 2H), 2.71 (sept, $J = 6.6$ Hz, 4H), 1.19–1.16 ppm (m, 24H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 162.6$, 162.3, 145.6, 137.9, 134.3, 132.7, 132.3, 131.2, 130.1, 130.0, 129.9, 129.1, 129.0, 128.4, 128.3, 125.3, 124.4, 124.3, 123.4, 29.3, 24.0 ppm; IR (KBr): $\tilde{\nu} = 1710$, 1671, 1596, 1504, 1466, 1444, 1418, 1388,

1340, 1250, 1197, 1146, 1010, 913, 733 cm⁻¹; MS TOF: *m/z* calcd for C₅₂H₄₄N₈O₄: 844.35; found: 844.4.

***N,N'*-Bis(2,6-diisopropylphenyl)-1,7-bis(pyrazol-1-yl)perylene-3,4,9,10-tetracarboxylic acid diimide (4)**: A mixture of pyrazole (136 mg, 2 mmol), anhydrous potassium carbonate (55 mg, 0.4 mmol), and [18]crown-6 (105 mg, 0.4 mmol) was stirred in toluene (50 mL) at room temperature and 1,7-dibromo-*N,N'*-bis(2,6-diisopropylphenyl)perylene-3,4,9,10-tetracarboxylic acid diimide (158 mg, 0.2 mmol) was added. The reaction mixture was heated at reflux under nitrogen with stirring for 12 h. After the system had cooled to room temperature, the solvent was removed under reduced pressure and the crude product was obtained. Purification was accomplished by using column chromatography on silica gel with CH₂Cl₂ to give **4** (148 mg, 88%). ¹H NMR (400 MHz, CDCl₃): δ = 8.82 (s, 2H), 8.44 (d, *J* = 8.0 Hz, 2H), 7.93 (d, *J* = 1.9 Hz, 2H), 7.84 (d, *J* = 1.9 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 4H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.72–6.70 (m, 2H), 2.73 (sept, *J* = 6.8 Hz, 4H), 1.17 ppm (d, *J* = 6.8 Hz, 24H); ¹³C NMR (100 MHz, CDCl₃): δ = 163.1, 162.7, 145.6, 143.3, 138.0, 133.4, 131.6, 131.2, 130.2, 130.1, 130.0, 129.9, 129.3, 128.5, 128.4, 124.2, 123.9, 122.8, 110.2, 29.3, 24.0 ppm; IR (KBr): $\tilde{\nu}$ = 1707, 1669, 1594, 1460, 1338, 1246, 1196, 1150, 745 cm⁻¹; MS TOF: *m/z* calcd for (C₅₄H₄₆N₆O₄): 842.35; found: 842.5.

Compound 7: Compound **6** (0.02 mmol) in CH₂Cl₂ (20 mL) was irradiated in sunlight for about 2 d. The solution became yellow, the solvent was removed by reduced pressure, and the crude product was obtained. Purification was accomplished by using column chromatography on silica gel with CH₂Cl₂ to give **7** (85%). ¹H NMR (400 MHz, CDCl₃): δ = 10.29 (s, 1H), 10.17 (s, 1H), 9.07 (s, 1H), 8.93 (s, 1H), 8.79 (d, *J* = 8.4 Hz, 1H), 8.65 (s, 1H), 8.56 (s, 1H), 7.56–7.53 (m, 2H), 7.41 (t, *J* = 8.0 Hz, 4H), 7.30 (d, *J* = 8.4 Hz, 1H), 2.79 (sept, *J* = 6.9 Hz, 4H), 1.24–1.18 ppm (m, 24H); IR (KBr): $\tilde{\nu}$ = 1716, 1676, 1602, 1462, 1363, 1334, 1266, 1013, 839, 815, 740, 713 cm⁻¹; MS TOF: *m/z* calcd for C₅₂H₄₂N₈O₄: 842.33; found: 842.4.

Compound 8: Compound **6** (0.02 mmol) in CH₂Cl₂ (20 mL) was irradiated in the sun for about 6 d. The solution became yellow, the solvent was removed by reduced pressure, and the crude product was obtained. Purification was accomplished by using column chromatography on silica gel with CH₂Cl₂ to give **8** (40%). ¹H NMR (400 MHz, CDCl₃): δ = 10.52 (s, 2H), 10.51 (s, 2H), 9.03 (s, 2H), 7.63–7.58 (m, 2H), 7.46 (d, *J* = 7.8 Hz, 4H), 2.95–2.85 (m, 4H), 1.26–1.19 ppm (m, 24H); IR (KBr): $\tilde{\nu}$ = 1715, 1675, 1509, 1463, 1320, 1256, 1180, 822, 746 cm⁻¹; HRMS (FAB⁺): *m/z* calcd for C₅₂H₄₀N₈O₄+H: 841.3251; found: 841.3251 [M+H]⁺.

Compound 3: Compound **2** (0.1 mmol) in CH₂Cl₂ (20 mL) was irradiated in the sun for about 3 h. The solvent was removed by reduced pressure and the crude product was obtained. Purification was accomplished by using column chromatography on silica gel with CH₂Cl₂ to give **3** (61 mg, 75%). ¹H NMR (400 MHz, CDCl₃): δ = 10.47 (s, 2H), 9.80 (s, 2H), 8.93 (s, 2H), 8.26 (s, 2H), 7.60 (t, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 4H), 2.95–2.80 (m, 4H), 1.27–1.23 ppm (m, 24H); IR (KBr): $\tilde{\nu}$ = 1715, 1677, 1606, 1508, 1465, 1443, 1329, 1256, 1189, 1032, 811 cm⁻¹; HRMS (FAB⁺): *m/z* calcd for C₅₄H₄₂N₆O₄+H: 839.3346; found: 839.3355 [M+H]⁺.

Compound 5: Compound **4** (0.02 mmol) in CH₂Cl₂ (20 mL) was irradiated in the sun for about 3 d. The solvent was removed under reduced pressure, and the crude product was obtained. Purification was accomplished by using column chromatography on silica gel with CH₂Cl₂ to give **5** (75%). ¹H NMR (400 MHz, CDCl₃): δ = 10.16 (s, 1H), 9.62 (s, 1H), 8.98 (s, 1H), 8.64 (d, *J* = 8.4 Hz, 1H), 8.52 (d, *J* = 1.8 Hz, 1H), 8.06 (s, 1H), 7.95 (s, 1H), 7.70 (d, *J* = 1.8 Hz, 1H), 7.58–7.51 (m, 2H), 7.42–7.37 (m, 4H), 6.99–6.88 (br, 1H), 6.84 (s, 1H), 2.88–2.73 (m, 4H), 1.23–1.17 ppm (m, 24H); IR (KBr): $\tilde{\nu}$ = 1713, 1674, 1600, 1520, 1458, 1407, 1336, 1249, 1198, 922, 814, 738 cm⁻¹; HRMS (FAB⁺): *m/z* calcd for C₅₄H₄₄N₆O₄: 840.3424; found: 840.3400 [M]⁺.

Compound 10: A mixture of imidazole (13.6 mg, 0.2 mmol), anhydrous potassium carbonate (5.5 mg, 0.04 mmol), and [18]crown-6 (10 mg, 0.04 mmol) was stirred in toluene (20 mL) at room temperature, and 1-bromo-*N,N'*-bis(2,6-diisopropylphenyl)perylene-3,4,9,10-tetracarboxylic acid diimide (15 mg, 0.02 mmol) was added. The reaction mixture was heated at reflux under nitrogen with stirring for 12 h. After the system had cooled to room temperature, the solvent was removed by reduced pressure, and the crude product was obtained. Purification was accom-

plished by using column chromatography on silica gel with CH₂Cl₂ to give **10** (12 mg, 78%). ¹H NMR (400 MHz, CDCl₃): δ = 10.32 (s, 1H), 9.54 (s, 1H), 9.30 (d, *J* = 8.2 Hz, 1H), 9.25 (d, *J* = 8.2 Hz, 1H), 9.12 (d, *J* = 8.2 Hz, 2H), 8.78 (s, 1H), 8.21 (s, 1H), 7.59–7.52 (m, 2H), 7.43–7.38 (m, 4H), 2.86–2.79 (m, 4H), 1.23–1.20 ppm (m, 24H); IR (KBr): $\tilde{\nu}$ = 1712, 1672, 1597, 1436, 1357, 1326, 1253, 1195, 1149, 838, 812, 741 cm⁻¹; HRMS (FAB⁺): *m/z* calcd for C₅₁H₄₂N₄O₄: 774.3206; found: 774.3208 [M]⁺.

Compound 11: A mixture of pyrazole (13.6 mg, 0.2 mmol), anhydrous potassium carbonate (5.5 mg, 0.04 mmol), and [18]crown-6 (10 mg, 0.04 mmol) was stirred in toluene (20 mL) at room temperature and 1-bromo-*N,N'*-bis(2,6-diisopropylphenyl)perylene-3,4,9,10-tetracarboxylic acid diimide (15 mg, 0.02 mmol) was added. The reaction mixture was heated at reflux under nitrogen with stirring for 12 h. After the system had cooled to room temperature, the solvent was removed under reduced pressure, and the crude product was obtained. Purification was accomplished by using column chromatography on silica gel with CH₂Cl₂ to give **11** (10 mg, 66%). ¹H NMR (400 MHz, CDCl₃): δ = 10.15 (s, 1H), 9.55 (s, 1H), 9.21–9.16 (m, 2H), 9.09–9.03 (m, 2H), 8.50 (d, *J* = 1.9 Hz, 1H), 7.66 (d, *J* = 1.9 Hz, 1H), 7.57–7.52 (m, 2H), 7.42–7.39 (m, 4H), 2.87–2.82 (m, 4H), 1.25–1.20 ppm (m, 24H); IR (KBr): $\tilde{\nu}$ = 1712, 1673, 1595, 1459, 1410, 1328, 1254, 1194, 914, 810, 744 cm⁻¹; HRMS (FAB⁺): *m/z* calcd for C₅₁H₄₂N₄O₄: 774.3206; found: 774.3209 [M]⁺.

Acknowledgements

This work was supported by the Major State Basic Research Development Program and the National Natural Science Foundation of China (grants 20531060, 10474101, 20418001, 20473102, and 20421101).

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Received: April 30, 2006

Published online: August 9, 2006