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Bis-*N*-annulated Quaterrylenebis(dicarboximide) as a New Soluble and Stable Near-Infrared Dye

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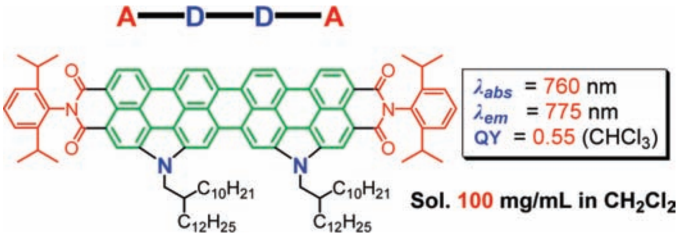
ABSTRACT



A new ladder-type bis-*N*-annulated quaterrylenebis(dicarboximide) (1) was synthesized, and it exhibits excellent solubility in common organic solvents, high molar absorptivity, and good stability. Moreover, it absorbs and emits light in the near-IR spectral region with a high fluorescence quantum yield. All these properties qualify it as a promising NIR dye for many applications.

Sunlight, the rich and green resource, possesses about 50% of its radiation intensity in the near-infrared (NIR) region ranging from 700 to 2000 nm. Thus, the development of dyes and pigments that function in the NIR spectral region is essential for diverse applications, such as optical recording, laser filter, NIR photography, bioassays, and medicine.[1,2] A recent rising interest is to use low band gap NIR dyes for solar cells,[3] bioimaging,[4] and two-photon absorption (TPA) based optical limiting at telecommunications wavelength.[5] For all of these applications, soluble and stable dyes which can absorb and/or emit light in the NIR region are highly desirable. However, many commercially available NIR dyes suffer from inevitable drawbacks due to their insufficient photostability.[6]

Rylenes and their dicarboxylic imide derivatives are key chromophores in dye chemistry due to their excellent chemical and photostability. Up to now, perylenebis(dicarboximide)s[7] and higher rylenes, namely terrylene,[8] quaterrylene,[9] pentarylene,[10] and hexarylene,[10] have been synthesized, and the higher order rylene bis(dicarboximide)s can

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serve as good NIR dyes due to extended π-conjugation. A general problem for the higher order rylene dyes is their poor solubility even though some bulky groups are attached to the *peri*-positions of the terminal naphthalene units. To further improve their solubility, substitution by phenoxy groups at the bay positions has been done, and materials with good solubility have been obtained.[9,10] One limit is that ring cyclization reactions sometimes suffer from the dealkylation of the phenoxy group under strong basic conditions.[9b] Alternative substitution groups at the bay positions of higher order rylene dyes are desired to facilitate an easy organic synthesis of highly soluble NIR dyes. In addition, the substituents with either electron-donating or electron-withdrawing character can further tune their electronic and spectral properties for applications such as n-channel FETs, solar cells, and laser absorbing dyes.[11]

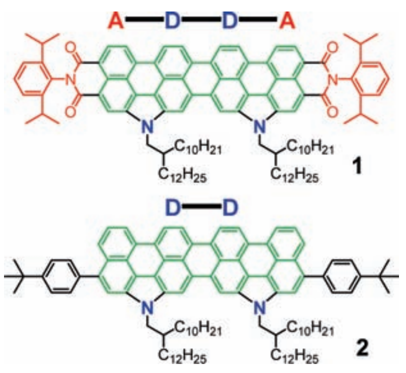

Figure 1. Molecular structures of bis-*N*-annulated quarterrylene (**2**) and quarterrylenebis(dicarboximide) (**1**).

N-Annulation of perylene[12] in which the nitrogen atoms are annulated at the bay position becomes one option for such a purpose because additional flexible alkyl chains can be easily introduced by alkylation reaction and thus improve the solubility. In addition, the electron-donating character of amines can increase the electron density of the entire π-system and lead to new opto-electronic properties. Wang et al. reported several *N*-annulated perylenes,[12b−e] and very recently, a bis *N*-annulated quaterrylene with good solubility was also synthesized.[12d] In parallel to those studies, in the past year we have been working on the synthesis of a bis-*N*-annulated quarterrylenebis(dicarboximide) such as compound **1** (Figure 1). The design is based on the following considerations: (1) The electron-withdrawing dicarboxylic imide groups can significantly lower the high-lying HOMO energy level of the respective *N*-annulated perylene and quarterrylenes, which are expected to be unstable upon long-term exposure to air and light. (2) The molecule **1** has a typical acceptor−donor−donor−acceptor (**A**−**D**−**D**−**A**) motif which may show large two-photon absorption in long IR wavelengths.[13] On the other hand, a bis-*N*-annulated quarterrylene such as molecule **2** has a donor−donor (**D**−**D**, Scheme 1) motif. (3) Substitution of the bulk 2,6-diisopropylphenyl groups on the imides and the attachment of the branched dove-tailed chains at the amine sites will largely improve the solubility of the quarterrylene dyes. In this paper, we report the successful synthesis of compound **1** which shows the desired photophysical and electrochemical properties. For comparison, compound **2** was also prepared.

The synthesis of compounds **1** and **2** is shown in Scheme 1. There are two major challenges for the synthesis of **1**: (1) the synthesis of *N*-annulated perylene dicarboxylic imide (NPDI) **6** and (2) the subsequent ring cyclization of the NPDI dimer **7**. Although perylene dicarboxylic imide (PDI) can be readily obtained by one-step reaction from the cheap perylene tetracarboxylic dianhydride,[14] there is no efficient way to synthesize NPDIs such as **6**. We and other researchers recently found that arenedicarboxylic anhydride could be prepared by Friedel−Crafts reaction of oxalyl chloride with active aromatic compounds such as anthracene followed by oxidation of the as-formed diketone to the carboxylic anhydride group in good yields.[15] Herein, this method was used, and the key intermediate compound **6** was prepared in a convenient synthetic route.

The synthesis commenced with *N*-alkylation reaction of the *N*-annulated perylene (NP) **3**[12] with a dove-tailed alkyl bromide[16] in the presence of KOH and KI to give **4** in 97% yield. Regioselective bromination of **4** with 1 equiv of NBS at 0 °C gave the monobrominated NP **5** in 80% yield. Friedel−Crafts reaction of **5** with oxalyl chloride promoted by $AlCl_3$ then generated an orange solid as a mixture containing different isomers of diketone compounds, which were directly converted to their corresponding anhydride compounds using oxone[15,15c] without purification. Separation of the NPDI **6** from other isomers was successful after the introduction of the 2,6-diisopropylaniline to the anhydride group with an overall yield of 48% for three steps. The precursor **7** was then prepared by Yamamoto coupling of **6** in a nearly quantitative yield. The last cyclization reaction was performed under different conditions such as (1) KOH in ethanol with glucose, (2) *tert*-BuOK/DBN in diglyme, (3) $FeCl_3$ in nitromethane and dichloromethane, and (4) K_2CO_3 in ethanolamine. It was found out that the first three methods all failed, and complicated mixtures were usually obtained probably due to the decomposition of NPDI units. Fortunately, method 4, using mild base K_2CO_3-promoted cyclization, worked well, and our target compound **1** was obtained in 35% yield. Compound **2** was prepared following a route similar to that

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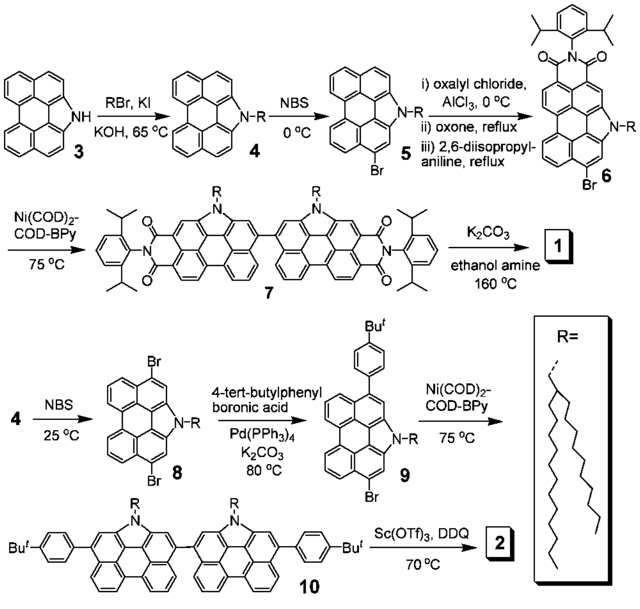
Scheme 1



found in the literature.[12d] Regioselective bromination of **4** with 2 equiv of NBS at room temperature gave the dibrominated NP **8** in 98% yield. Suzuki coupling reaction of **8** with 1 equiv of *tert*-butylphenylboronic acid afforded monosubstituted NP compound **9** in 44% yield. Yamamoto coupling of **9** provided the precursor **10** in a nearly quantitative yield, which was finally cyclized into the bis-*N*-annulated quarterrylene **2** in 62% yield by using a Sc(OTf)$_3$-DDQ system.[12d]

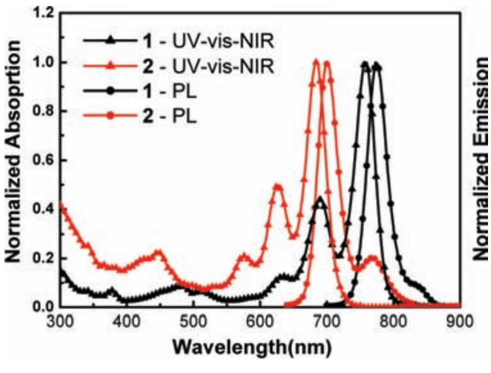


Figure 2. Normalized UV−vis−NIR absorption spectra (3×10^{-6} M) and photoluminescence spectra (4×10^{-7} M) of compounds **1** and **2** in chloroform.

Both compounds **1** and **2** are highly soluble in common organic solvents, and this allows us to perform various characterizations in solution. In particular, dye **1** has a solubility of over 100 mg per mL in dichloromethane at room temperature, which is much higher than the quarterrylenebis(dicarboximide)s without bay substitution.[9b] The high solubility of **1** can account for the introduction of two bulk 2,6-diisopropylphenyl groups which inhibit the formation of π-stacks,[9b] the two dove-tailed alkyl chains, and the bent structure as disclosed by the calculated geometric structure (Figure S6 in the Supporting Information). Both dyes exhibit a deep green color in solution, their UV−vis−NIR absorption and fluorescence spectra recorded in chloroform are shown in Figure 2, and the data are collected in Table 1. Dye **1** exhibits intense absorption in the NIR spectral region with an absorption maximum at 760 nm, together with two shoulders at 690 and 632 nm, which are similar to the nonfunctionalized quarterrylene ($\lambda_{\text{abs, max}} = 764$ nm).[9b] The molar extinction coefficient (ε) of **1** is extremely high with $\varepsilon_{\max} = 259540$ M^{-1} cm^{-1} at 760 nm. In comparison, compound **2** without electron-withdrawing dicarboxylic imide groups shows absorption peaks at 685, 628, and 575 nm with $\varepsilon_{\max} = 90080$ M^{-1} cm^{-1}. A large bathochromic shift of 75 nm was observed for **1** compared with **2**, owing to the substitution by electron-withdrawing dicarboxylic imide groups in **1** which leads to a convergence of HOMO−LUMO energy gap as previously calculated.[13a,17] Both **1** and **2** display very small Stokes shifts (255 and 313 cm^{-1}, respectively) due to the rigid and planar quarterrylene structure (Figure S6, Supporting Information). The photoluminescence quantum yields (Φ) of dyes **1** and **2** were determined according to an optically dilute method ($A < 0.05$) by using cardiogreen dye (λ_{abs} (max) = 780 nm, $\Phi = 0.13$ in DMSO) as a standard.[18] The Φ values of 0.55 and 0.83 were obtained for **1** and **2**, respectively, and these values are higher than for other quaterrylene compounds.[12d,19] Time-dependent DFT calculations (B3LYP/6-31G**) predict that compounds **1** and **2** will show intense absorption in the NIR region with maxima at 708.5 and 663.4 nm and large oscillator strengths with $f = 1.7567$ and 1.5452, respectively (see the Supporting Information). These data agree well with our experimental results and explain the observed large ε values.

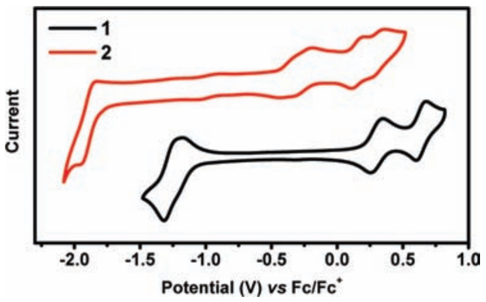


Figure 3. Cyclic voltammograms of compounds **1** and **2** in dichloromethane with 0.1 M Bu$_4$NPF$_6$ as supporting electrolyte, AgCl/Ag as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and scan rate at 50 mV/s. Fc/Fc$^+$ was used as internal reference.

The electrochemical properties of compounds **1** and **2** were investigated by cyclic voltammetry (CV) in dry DCM (Figure

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Table 1. Summary of Photophysical and Electrochemical Properties of Compound **1** and **2**[a]

compd	λ_{abs} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	λ_{em} (nm)	QY	E_{ox}^1 (V)	E_{ox}^2 (V)	E_{ox}^3 (V)	E_{red} (V)	HOMO (eV)	LUMO (eV)	E_g (eV)
1	632 690 760	259540	775	0.55	0.30	0.64		−1.26	−5.10	−3.54	1.56
2	575 628 685	90080	700	0.83	−0.29	0.16	0.32	−1.89	−4.51	−2.91	1.60

[a] E_{ox}^n and E_{red}^n are half-wave potentials for respective redox waves with Fc/Fc$^+$ as reference. HOMO and LUMO energy levels were calculated from the first oxidation and reduction waves according to the equations HOMO = $-(4.8 + E_{ox}^1)$ and LUMO = $-(4.8 + E_{red}^1)$.[20]

3 and Table 1). The cyclic voltammogram of **1** exhibits two reversible oxidation waves with half-wave potentials (E_{ox}^n) at 0.30 and 0.64 V (vs Fc/Fc$^+$), while three oxidative waves were observed for **2**, with E_{ox}^n at − 0.29, 0.16, and 0.32 V (vs Fc/Fc$^+$). The very low first half-wave oxidation potential (− 0.29 V) of **2** indicates a highly electron-rich character of this π-conjugated system due to the electron-donating property of the amines. A high-lying HOMO energy level of − 4.51 eV was calculated for **2** based on the E_{ox}^1, and this implies that compound **2** can be easily oxidized by many oxidants.[20] In fact, we found that the green solution of **2** in toluene became dark in a few hours when the solution was exposed to ambient conditions, and significant decomposition was observed as followed by UV−vis−NIR spectroscopic measurements. In contrast, the first oxidative half-wave potential of **1** with electron-withdrawing imide groups appears at a much higher potential (0.30 V) with a HOMO energy level of −5.10 eV. As a result, the UV−vis−NIR absorption spectrum of **1** in toluene does not show any change upon exposure to ambient air and light for weeks and even under irradiation of 4 W UV lamp (emitting at 254 nm) for 5 days, suggesting a good photostability of dye **1**, and this is important for practical applications. Compound **1** also exhibits two reversible reduction waves around −1.26 V which are overlapped together but distinguishable by differential pulse voltammetry. Accordingly, a LUMO energy level of −3.54 eV was calculated, indicating a high electron affinity of dye **1** due to the carboximide substitution. In addition, one quasi-reversible reduction wave was also observed for **2** at a negative potential of −1.89 V, indicating that although this molecule is electron-rich, it is still possible to store negative charge by electron delocalization along the large π-conjugated framework. Compared with **2**, molecule **1**, having an A−D−D−A motif, exhibits a smaller band gap (1.56 eV), which is in agreement with their absorption spectra.

In summary we have described the efficient synthesis of a new NIR dye, the bis-*N*-annulated quarterrylenebis(dicarboximde) **1**, which shows remarkable properties such as excellent solubility, high molar absorptivity, NIR absorption and emission, high fluorescence quantum yield, and good photostability in comparison with the electron-rich analogue **2**. Further studies on their NLO properties such as TPA and synthesis of higher order *N*-annulated rylene carboximides are in progress, and this research will likely lead to useful materials for applications such as optical limiting[5] and photovoltaic windows.[21]

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Supporting Information Available: Experimental details and characterization data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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