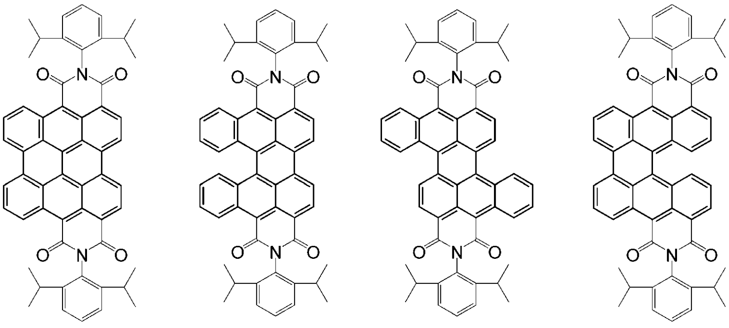
DOI: 10.1002/chem.200901398

Bisanthracene Bis(dicarboxylic imide)s as Soluble and Stable NIR Dyes

Jun Hong Yao, Chunyan Chi, Jishan Wu,* and Kian-Ping Loh*[a]

Dyes with near-infrared (NIR) absorption and/or emission have shown promising applications for optical recording, laser filter, thermal writing display, NIR photography, bioimaging, photodynamic therapy, and solar cells.[1,2] Most of the commercially available NIR dyes such as polymethine dyes (dominated by cyanine dyes), quinone dyes, azo dyes, charge transfer salts, radical dyes, and phthalocyanine dyes usually suffer from either poor thermal and photostability or low solubility which limit their practical applications. Alternatively, dyes based on polycyclic aromatic hydrocarbons (PAHs) showed excellent stability and thus they can be used as key building blocks for the design of stable and soluble NIR dyes with tunable light absorption and emission wavelength. One class of widely investigated dyes based on PAHs are rylenes and their dicarboxylic imide derivatives, which serve as key chromophores in dyestuff chemistry due to their excellent chemical and photostability.[3] To achieve intense absorption/emission in NIR region, a lot of work has been done to extend the π-conjugation along the long axis of rylene molecules and stable polyaromatic NIR dyes such as quarterylene, pentarylene and hexarylene bis(dicarboxylic imide)s have been reported.[4] Although the extension along the long axis is an efficient way to approach NIR absorption, the syntheses of higher order soluble rylene dyes are very cumbersome. Theoretical calculations also predicted that lateral extension of rylene dyes by fusion of additional benzene rings will provide an alternative method to extend the π-conjugation and result in NIR absorption,[5] however, until today, there are only a few reports on the effective expansion of π-conjugation along the short axis of rylene molecules mainly due to practical synthetic challenges. In this communication, we report a series of soluble and stable NIR dyes based on laterally expanded bisanthracene bis(dicarboxylic imide)s **M1**–**M4** (Scheme 1), which can also be regarded as dibenzoperylene derivatives. Optical and electrochemical measurements of these dyes indicated that all of these dyes showed intense absorption between 600 and 1000 nm with significant lower band gaps in comparison with the perylene tetracarboxylic diimide (PDI), suggesting that lateral extension is indeed an efficient way to obtain polyaromatic NIR dyes.



M1 **M2** **M3** **M4**

Scheme 1. Structures of bisanthene bis(dicarboxylic imide) (**M1**) and partially cyclized bisanthene bis(dicarboxylic imide)s (**M2**–**M4**).

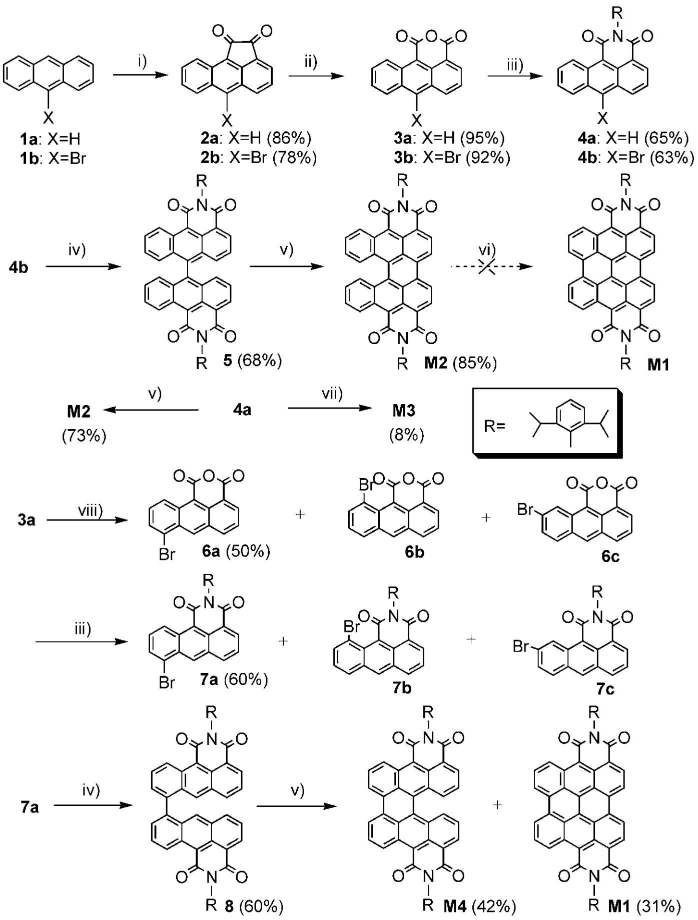
The fully fused anthracene dimer, the so-called bisanthene, has been synthesized with absorption maximum at 662 nm, indicating its great potential as an NIR dye building block. However, it showed low solubility and very poor stability upon exposure to air due to its high lying HOMO energy level.[7] Therefore, herein electron-withdrawing dicarboxylic imide groups were introduced to improve its stability as well as solubility. The partially cyclized bisanthracene bis(dicarboxylic imide)s, aceanthrene green,[7,8] has ever been synthesized and used as textile dyes and pigments with NIR absorption peak at 701 nm. One *cis*-isomer in which H is attached to the N atoms was also prepared but it co-existed with the *trans*-isomer as a mixture. Nevertheless, the most desired structure, that is, fully cyclized bisanthene bis(dicarboxylic imide)s **M1** is still unknown although its at-

---

[a] Dr. J. H. Yao, Dr. C. Chi, Prof. J. Wu, Prof. K.-P. Loh
Department of Chemistry
National University of Singapore
3 Science Drive 3 (Singapore)
Fax: (+65) 6779-1691
E-mail: chmwuj@nus.edu.sg
chmlohkp@nus.edu.sg

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901398.

tractive properties have been theoretically predicted 14 years ago.[5] Herein we report the successful synthesis of this interesting compound which showed remarkable NIR absorption with absorption maximum at 830 nm (i.e., 168 and 130 nm red-shift compared with the parent bisanthene and aceanthrene green, respectively). In addition, the previously reported synthesis of aceanthrene green dyes/pigments was mainly done in melted KOH (ca. 220 °C) followed by oxidation in air or by H_2O_2, and the yields were usually low and most functional groups can not survive under so harsh conditions.[7,8] Therefore, improved synthetic method has to be developed to obtain sufficient materials for practical applications. For this reason, the partially fused bisanthracene bis(dicarboxylic imide)s **M2**–**M4** with different linking modes were also prepared in a more efficient way. The compounds obtained can be used to understand the effect of geometrical structure on physical properties by comparing with the fully cyclized compound **M1**. For all molecules, bulky 2,6-diisopropylaniline units were introduced to improve their solubility.



Scheme 2. Synthetic route for compounds **M1**–**M4**: i) oxalyl chloride, $AlCl_3$, CS_2, 0 °C; ii) oxone, methanol, reflux; iii) 2,6-diisopropylaniline, propionic acid, reflux; iv) [Ni(cod)$_2$]/COD/BPy, DMF, toluene, 80 °C; v) *t*BuOK, DBN, diglyme, 130 °C; vi) $FeCl_3$, CH_3NO_2, CH_2Cl_2; vii) melted KOH, then air; viii) Br_2, conc. H_2SO_4, RT. BPy = bipyridine.

Scheme 2 outlines the synthetic route for compounds **M1**–**M4**. The synthesis started from Friedel–Crafts reactions of anthracene (**1a**) or 9-bromoanthracene (**1b**) with oxalyl chloride to provide the aceanthrylene 1,2-diones[9] (**2a** and **2b**, respectively) which were subsequently oxidized to the carboxylic acid anhydrides (**3a** and **3b**, respectively) by oxone in high yields. The carboxylic anhydride was usually prepared first by oxidative ring-opening reaction by using H_2O_2 in NaOH solution and followed by ring-closing reaction in acetic anhydride.[9] Herein, we developed a simple, one-pot synthesis of the anthracene carboxylic anhydride from the respective aceanthrylene 1,2-diones by using a modified procedure.[10] Reactions between **3a** or **3b** with 2,6-diisopropylaniline gave the corresponding imides (**4a** and **4b**). The anthracene dicarboxylic imide dimer **5** was then synthesized by [Ni(cod)$_2$]-mediated Yamamoto homocoupling of **4b** and this was followed by *t*BuOK- and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN)-mediated cyclization reaction[11] to afford the desired *cis*-bisanthracene bis(dicarboxylic imide)s **M2** in 85 % yield. This is also the first efficient synthesis of the pure *cis*-isomer of *aceanthrene green* dyes. Unfortunately, compound **M2** cannot be further cyclized into the fully fused bisanthene carboximides **M1** under various cyclization conditions such as $FeCl_3$-mediated oxidative cyclodehydrogenation probably due to the strong electron-withdrawing effect of the imide groups which deactivated the reactive sites on the aromatic rings.[12] The *trans*-isomer **M3** was obtained in 8 % yield by heating the anthracene dicarboxylic imide **4a** in melted KOH according to a reported method.[7,8] It is interesting that treatment of **4a** using *t*BuOK and DBN in diglyme selectively gave the *cis*-isomers **M2** in 73 % yield and the detailed mechanisms of the selectivity are still under investigation. This simple method provided an efficient synthesis of soluble aceanthrene green *cis*-isomer in large scale. To prepare the target compound **M1**, the monobromo-substituted anthracene dicarboxylic imide **7a** was first synthesized. The key step was the bromination of **3a** in concentrated sulfuric acid which unavoidably gave a mixture of three isomers **6a–c** consisting of about 50 % the desired isomer **6a**. Separation of the compound **7a** from other isomers (**7b** and **7c**) was successful after the attachment of the 2,6-diisopropylaniline groups. The dimer **8** was then prepared by a similar Yamamoto coupling and followed by *t*BuOK- and DBN-mediated cyclization reaction. Both partially fused compound **M4** and fully fused **M1** were separated in pure forms with reasonable yields. The chemical structures and purity of compounds **M1**–**M4** were verified by ^{1}H NMR, ^{1}H,^{1}H-COSY NMR, ^{13}C NMR, mass spectroscopy and elemental analysis (Supporting Information).

M1–**M4** have very good solubility in common organic solvents such as CH_2Cl_2 and THF and they showed intense absorptions in NIR regions with absorption maximum at 830 nm ($\varepsilon = 15\,000\,\text{M}^{-1}\text{cm}^{-1}$), 697 nm ($\varepsilon = 47\,000\,\text{M}^{-1}\text{cm}^{-1}$), 697 nm ($\varepsilon = 38\,000\,\text{M}^{-1}\text{cm}^{-1}$), and 685 nm ($\varepsilon = 27\,000\,\text{M}^{-1}\text{cm}^{-1}$) for **M1**, **M2**, **M3** and **M4**, respectively (Figure 1). The absorption peak of 830 nm observed for **M1** suggested that it could be used as laser absorbing dye which

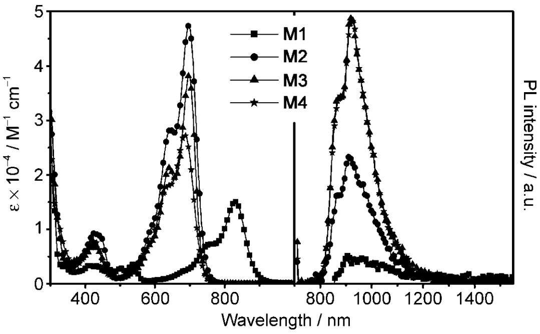


Figure 1. UV/Vis-NIR absorption and photoluminescence spectra of compounds **M1**–**M4** in CH_2Cl_2.

can absorb the light from the commercial semiconductor laser that emits light at 830 nm. This wavelength is also same to the absorption maximum of pentarylene tetracarboxylic diimide which contains five fused naphthalene units and required multiple-step synthesis.[4] Compared with PDI (λ_{abs}(max) = 526 nm), the laterally expanded molecule **M1** exhibited a remarkable 305 nm red-shift, suggesting that the lateral extension of π-conjugation is a more efficient way to obtain NIR absorption than by extension along the long axis. The 168 nm red-shift of **M1** in comparison with the parent bisanthene can be ascribed to the substitution by electron-withdrawing dicarboxylic imide groups which lead to a convergence of HOMO–LUMO energy gap as previously calculated.[5,13] The relatively lower ε value of **M1** compared with other rylene imides has been theoretically explained by Feng et al.[13] The partially fused dimers **M2**–**M4** showed a dark green color in solution and exhibited similar absorption bands. The absorption band of the fully fused bisanthene carboximide **M1** displayed a significant red-shift by more than 130 nm due to extended π-conjugation. Compounds **M2**–**M4** showed similar NIR photoluminescence bands with emission maximum at 923 nm for **M3** and **M4** and 912 nm for **M2**. Compound **M1** only exhibited weak photoluminescence. The photoluminescence quantum yields[14] of dyes **M2**–**M4** are less than 0.5 % which was normally observed for many NIR absorbing dyes. However, for many applications such as laser filter and solar cell, photoluminescence is not necessary and even should be avoided.

Solutions of **M1**–**M4** are stable upon exposure to air due to the attachment of electron-withdrawing dicarboxylic imide groups. Cyclic voltammetry (CV) was applied to examine their electrochemical behaviors as well as to determine their energy levels (Figure 2). All compounds showed one reversible oxidation at potentials above 1.1 V and two reversible one-electron reductions at potential below −0.11 V (vs. AgCl/Ag). The two-reduction processes indicate that the molecules can be reduced into stable anion and dianion which are stabilized by the two imide groups. At the same time, these large π-conjugated systems can also stabilize the oxidized cationic species. The fully fused dimer **M1** has a narrow band gap (1.26 eV) and can undergo charge transfer readily. The other partially fused molecules **M2**–**M4** displayed relatively larger band gaps (1.52–1.57 eV). The reduction and oxidation onset potentials also varied depending on the linking modes and more detailed data of redox potentials, energy levels and band gaps was listed in Table 1. The high electron affinity (the LUMO energy level) of these molecules also suggested that these imide-substituted polycyclic aromatic compounds, and in particular the fully planar bisanthene carboximide, could be used as building blocks to construct n-type semiconductors for electronic devices such n-channel field effect transistors and solar cells. Of course, appropriate modifications on the substituents are necessary to control their molecular order in thin film for these purposes.

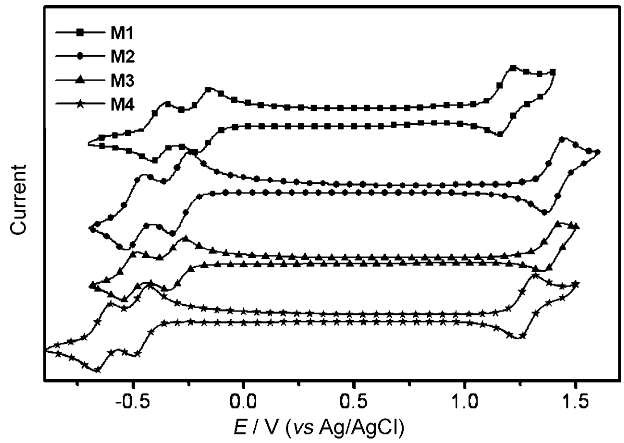


Figure 2. Cyclic voltammograms of compounds **M1**–**M4** in dry CH_2Cl_2, Bu_4NPF_6 (0.1 M) as supporting electrolyte, gold disk as working electrode, Pt as counter electrode and AgCl/Ag as reference electrode, scan rate at 0.1 $V s^{-1}$.

Table 1. Summary of electrochemical properties of compounds **M1**–**M4**. E_{ox}, E^1_{red} and E^2_{red} are the half-wave potentials for respective redox waves with E (Fc^+/Fc) as reference. Fc^+/Fc was used as internal reference and under our experimental conditions, E (Fc^+/Fc) = 0.42 V vs Ag/AgCl.

Compound	E_{ox} [V]	E^1_{red} [V]	E^2_{red} [V]	HOMO[a] [eV]	LUMO[b] [eV]	E_g [eV]
M1	0.74	−0.62	−0.84	−5.53	−4.27	1.26
M2	0.94	−0.74	−0.95	−5.67	−4.15	1.52
M3	0.95	−0.75	−0.96	−5.68	−4.16	1.52
M4	0.84	−0.91	−1.08	−5.57	−4.00	1.57

[a] HOMO energy level was calculated from the onset of oxidation wave. [b] LUMO energy level was calculated from the onset of the first reduction wave. The energy levels were calculated by using the following equations: HOMO = $-(4.8 + E_{ox})$ (1), LUMO = $-(4.8 + E_{red})$ (2).

In summary, a series of soluble and stable bisanthracene bis(dicarboxylic imide)s were synthesized and their optical and electrochemical properties were studied. The fully planar bisanthene carboximide **M1** was synthesized as stable compound for the first time and it showed interesting NIR absorption properties. The *cis*-isomer of aceanthrene green (**M2**) was also prepared in pure form by two simple methods in high yields. Our experiments proved that lateral extension of rylene molecules was an effective way to shift the absorption into near infrared region in a fast mode. The intense NIR absorptions suggested that they could be used as useful dyes for many applications such as NIR laser protection glasses. In addition, the n-type character and the intense NIR absorption of these dyes qualify them as either semiconductors or dyes for applications such as n-channel field-effect transistors,[15] bulk hetero-junction solar cells[16] and NIR dyes-sensitized photovoltaic devices in the future.[17] Furthermore, the synthetic strategy also provided a valuable clue to the synthesis of soluble and stable higher order laterally expanded periacence compounds,[18] which are supposed to have even longer absorption and remarkable electronic and photophysical properties.

Acknowledgements

This work was financially supported by Singapore NRF Competitive Research Program ("Graphene-related Materials and Devices"), DSTA DIRP project (DSTA-NUS-DIRP/2008/03) and the NUS Young Investigator Award (R-143-000-356-101).

Keywords: anthracenes · hydrogenation · dyes/pigments · rylenes

---

[1] J. Fabian, H. Nakanzumi, M. Matsuoka, *Chem. Rev.* **1992**, *92*, 1197–1226.
[2] J. Fabian, R. Zahradnik, *Angew. Chem.* **1989**, *101*, 693–710; *Angew Chem. Int. Ed. Engl.* **1989**, *28*, 677–828.
[3] A. Herrmann, K. Müllen, *Chem. Lett.* **2006**, *35*, 978–985.
[4] N. G. Pschirer, C. Kohl, F. Nolde, J. Qu, K. Müllen, *Angew. Chem.* **2006**, *118*, 1429–1432; *Angew. Chem. Int. Ed.* **2006**, *45*, 1401–1404.
[5] D. Désilets, P. M. Kazmaier, R. A. Burt, *Can. J. Chem.* **1995**, *73*, 319–324.
[6] a) S. M. Arabei, T. A. Pavich, *J. Appl. Spectrosc.* **2000**, *67*, 236–244; b) H. Kuroda, *J. Chem. Soc.* **1960**, 1856–1857; c) E. Clar, *Chem. Ber.* **1948**, *81*, 52–63.
[7] D. Désilets, P. M. Kazmaier, R. A. Burt, G. K. Hamer, *Can. J. Chem.* **1995**, *73*, 325–335.
[8] H. Langhals, G. Schonmann, K. Polborn, *Chem. Eur. J.* **2008**, *14*, 5290–5303.
[9] S. M. Sami, R. T. Dorr, A. M. Solyom, D. S. Alberts, W. A. Remers, *J. Med. Chem.* **1995**, *38*, 983–993.
[10] J. Yan, B. R. Travis, B. Borhan, *J. Org. Chem.* **2004**, *69*, 983–993.
[11] T. Sakamoto, C. Pac, *J. Org. Chem.* **2001**, *66*, 94–98.
[12] a) J.-S. Wu, M. D. Watson, L. Zhang, Z. Wang, K. Müllen, *J. Am. Chem. Soc.* **2004**, *126*, 177–186; b) J.-S. Wu, W. Pisula, K. Müllen, *Chem. Rev.* **2007**, *107*, 718–747.
[13] Y. Zhao, A.-M. Ren, J.-K. Feng, C.-C. Sun, *J. Chem. Phys.* **2008**, *129*, 014301.
[14] The photoluminescence quantum yields of **M1**–**M4** in chloroform were estimated by using fluorescein as standard. However, due to the low luminescence intensity and the lack of efficient NIR dye as standard, the value was roughly estimated as less than 0.5% for all cases.
[15] A. S. Molinari, H. Alves, Z.-H. Chen, A. Facchetti, A. F. Morpurgo, *J. Am. Chem. Soc.* **2009**, *131*, 2462–2463.
[16] S. Günes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.* **2007**, *107*, 1324–1338.
[17] P. Y. Reddy, L. Gribabu, C. Lyness, H. J. Snaith, C. Vijaykumar, M. Chandrasekharam, M. Lakshmikantam, J.-H. Yum, K. Kalyanasundaram, M. Grätzel, M. K. Nazeeruddin, *Angew. Chem.* **2007**, *119*, 377–380; *Angew. Chem. Int. Ed.* **2007**, *46*, 373–376.
[18] a) D.-E. Jiang, B. G. Sumpter, S. Dai, *J. Chem. Phys.* **2007**, *127*, 124703; b) D.-E. Jiang, S. Dai, *Chem. Phys. Lett.* **2008**, *466*, 72–75; c) M. Bendikov; F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891–4945; F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891–4945.

Received: May 26, 2009