Amino-substituted rylene dicarboximides and their quinoidal charge delocalization after deprotonation†

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A novel approach towards NIR absorption, including the deprotonation and subsequent quinoidal charge delocalization of amino-substituted rylene dicarboximides, is presented.

Organic colorants possessing near-infrared (NIR) absorption properties have received much attention in the last decade because of their extensive high-tech applications, such as energy management, photovoltaics, biosensing, optical data storage and telecommunications.[1,2] Since a comprehensive review on NIR dyes appeared in 1992,[2] many novel NIR chromophores have been developed.[3] Oligomeric porphyrin ribbons with an absorption between 1500 and 2500 nm,[4] and a quinoidal porphyrin dimer absorbing at 1080 nm[5] serve as outstanding examples. Quinoidal oligothiophenes that have an absorption above 1000 nm and quinoidal oligophenylene radical cations that absorb at 1302 nm have also been described.[6,7] Generally, the formation of quinoidal structures (*e.g.* having *para*-benzoquinone-type conjugated double bonds) lowers the HOMO–LUMO energy gap of the molecule, which shifts the NIR absorption bathochromically.

Perylene imide dyes and their homologues (Fig. 1, **1a–e**) are known for their thermal and photochemical stability, intense absorption and easy functionalization.[8] Perylene and terrylene bis(dicarboximide)s **1a** and **1b** absorb in the visible region (520 and 660 nm, respectively),[9] whereas for the higher rylene homologues, quaterrylene **1c**,[10] pentarylene **1d** and hexarylene **1e** bis(dicarboximide)s,[11] the absorption is shifted bathochromically into the NIR region (760, 877 and 950 nm, respectively). The combination of a core-extension with a push–pull effect,[12] or with non-planarity of the polyaromatic core,[13] allowed for the preparation of new rylene NIR dyes with an absorption above 1000 nm. Some radical cations or anions of perylene bis(dicarboximide)s also exhibit NIR absorption bands.[14]

In this Communication, we report a novel approach towards NIR absorption, which combines three known methods: core-extension, a push–pull effect and quinoidization. Rylene dicarboximides (RIs) **2–5** (from naphthalene to quaterrylene), substituted with amino groups at the *peri*-positions (Fig. 1), have been synthesized. Their deprotonation in the presence of base resulted in the formation of quinoidal structures **2′–5′** (Scheme 1), which have intense absorption bands at 566, 826, 1008 and 1186 nm, respectively.

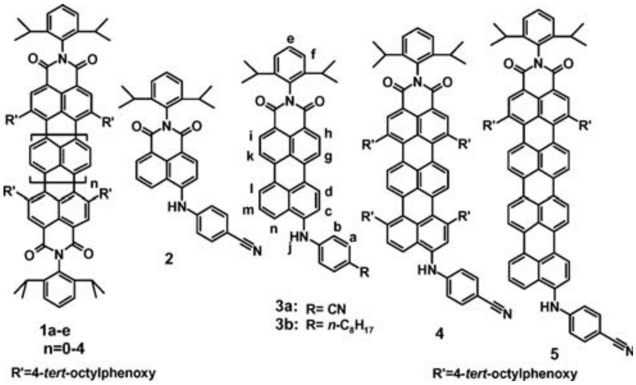
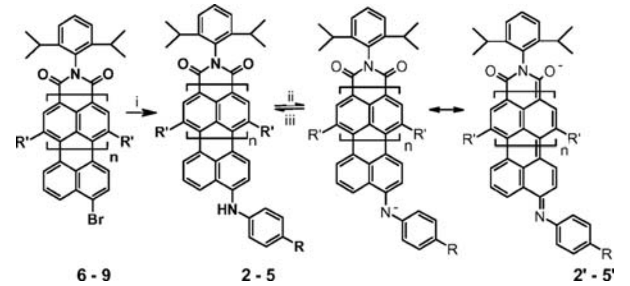


Fig. 1 The structures of rylene bisimides **1a–e** and monoimides **2–5**.

Syntheses of amino-substituted RIs **2–5** were achieved in high yields by the palladium-catalyzed coupling of precursors **6–9**,[9,10,15,16] bearing a bromo substituent at a free *peri*-position, with 4-aminobenzonitrile or 4-octylaniline under Buchwald conditions (Scheme 1).[17] All compounds were characterized by ^{1}H NMR, ^{13}C NMR and FTIR spectroscopy, as well as by elemental analysis (see ESI†). The corresponding deprotonated structures, **2′–5′**, were obtained quantitatively upon the treatment of acetone solutions of **2–5** with equimolar amounts of solid *t*-BuONa or NaOH. ^{1}H NMR spectra confirmed their complete conversion.



Scheme 1 *Reagents, conditions and yields:* (i) 4-aminobenzonitrile (for **2**, **3a**, **4** and **5**) or 4-octylaniline (for **3b**), $Pd_2(dba)_3$, tris-*tert*-butylphosphine, *t*-BuONa, toluene, 80 °C, 12 h; yields: **2** 95%, **3a** 84%, **3b** 77%, **4** 55%, **5** 53%; (ii) *t*-BuONa or NaOH (1 equiv.), acetone, RT, quantitative; (iii) 1 M HCl (1 equiv.), acetone, RT, quantitative. R′ = H or 4-(*tert*-octyl)phenoxy.

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^1H–^1H COSY NMR spectra of **3a′** and **3b′** were assigned using NOE NMR experiments, which allowed the pairs H_d/H_g and H_l/H_k to be unambiguously distinguished (see ESI†). The ^1H NMR spectrum of **3b′** was taken as an example for structural analysis here, due to its better solubility as a result of its long alkyl chains (ESI Fig. S3 and Table S1†). (i) The N–H proton of **3b** showed a singlet at 8.12 ppm, while no N–H signal was detected after treatment with base, which is indicative of deprotonation. (ii) The signals of H_c, H_d, H_g and H_h shifted dramatically upfield after deprotonation, from 7.38, 8.54, 8.50 and 8.42 ppm to 6.52, 7.94, 7.48 and 7.99 ppm, respectively, while the signals of H_i, H_k, H_l and H_m only shifted slightly. Thus, carbon atoms C_c, C_d, C_g and C_h have a higher electron density after deprotonation, which is obviously delocalized from the negative charge of the N-atom. (iii) Normally, the H–H coupling constants (^3J) for the perylene core are less than 8.5 Hz,[18] whereas the coupling constants for H_c/H_d and H_g/H_h after deprotonation are much higher, about 10.0 and 9.0 Hz, respectively. The higher H–H coupling constants suggest an enhancement of the double bond character of the pairs C_c/C_d and C_g/C_h.[19–22] (iv) The signal of H_n was unexpectedly shifted downfield by 0.35 ppm, which can be attributed to the vicinity of the newly formed C=N double bond. All of these results clearly confirm the formation of a novel quinoidal charge delocalization. Similar NMR data have already been described for a naphthalene imide treated with base, but this was not attributed to a quinoidal structure.[23]

The imide structure of rylene dyes undergoes hydrolysis under strongly basic conditions to give the anhydride structure after work-up.[17] However, compound **3b′** was found to be surprisingly stable when refluxed in 2-propanol with an excess of NaOH for 8 hours. This is additional evidence that the negative charge is further delocalized into the imide structure, which stabilizes it against nucleophilic attack. Actually, the electron-withdrawing effect of the imide group is the key driving force for negative charge delocalization. The mechanism of quinoidal structure formation can be described as follows (Scheme 1): the N–H proton is removed by the strong base and the quinoidal structure is formed where the negative charge is delocalized on the imide structure and is stabilized by the Na^+ counterion. The same process could also be accomplished in polar solvents such as THF and ethanol, while no conversion was observed in non-polar solvents such as toluene.

The amination of imides **6–9** introduces a push–pull effect into the molecules, inducing a bathochromic shift (16–91 nm). It is evident that the push–pull effect decreases from dye **2** to **5** due to the increasing size of the π-system (Fig. 2 and Table 1). Most interestingly, dyes **2′–5′** possess quinoidal charge delocalization that results in significant bathochromic shifts in their NIR absorption. Compounds **2**, **3a**, **3b**, **4** and **5** showed absorption maxima (λ_{max}) at 431 (ε = 21 300), 550 (ε = 34 800), 596 (ε = 35 200), 668 (ε = 41 900) and 751 (ε = 51 200) nm, respectively (Fig. 2 and Table 1). After the quinoidization of **2**, the absorption maximum shifted from 431 to 566 nm (ε = 28 300) in the visible region.[14] Higher homologues of **2′**, **3a′** and **4′**, exhibited a remarkable NIR absorption at 826 (ε = 90 400) and 1008 (ε = 132 200) nm. The wavelength for **4′** is comparable to that of hexarylene and dibenzopentarylene bis(dicarboximide)s,[11,13] but the molecular size is much smaller. The quinoidization of dyes **2–4** was accompanied by a significant increase in the magnitude of their extinction coefficients. Despite the fact that dye **5′** displayed a giant bathochromic shift of 435 nm, showing a peak at 1186 nm, its ε value of 65 100 was only slightly higher than that for the starting dye, **5**, presumably due to the aggregation of quaterrylene dyes in solution.[16] In contrast to the push–pull effect, the quinoidal structure increased the value of bathochromic shifts, Δλ, with the enlargement of the π-system, from 135 nm in the pair **2**/**2′** to 435 nm in the pair **5**/**5′**.

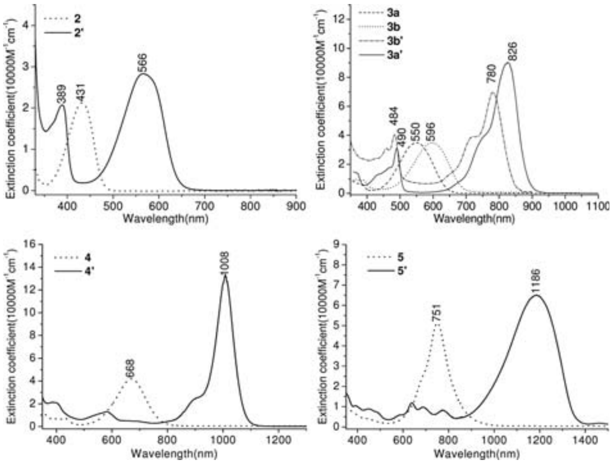

Fig. 2 UV-Vis–NIR absorption spectra of **2**, **3a**, **3b**, **4** and **5**, and their deprotonated forms **2′**, **3a′**, **3b′**, **4′** and **5′**.

Table 1 Absorption maxima for rylene dicarboximides **6–9**, amino substituted RIs **2–5** and their quinoidal forms **2′–5′**

		Push-pull effect →	Quinoidization →	
RIs	RI–Br (**6–9**) λ_{max}/nm	RI–NR (**2–5**) λ_{max}/nm ($\Delta\lambda_{max}$/nm)	RI–NR (**2′–5′**) λ_{max}/nm ($\Delta\lambda_{max}$/nm)	
Naphthalene	340	431 (91)	566 (135)	Core-extension ↓
Perylene[a]	510	550 (40)[a]	826 (276)[a]	
Perylene[b]	510	596 (86)[b]	780 (184)[b]	
Terrylene	645	668 (23)	1008 (340)	
Quaterrylene	735	751 (16)	1186 (435)	

[a] Data for **3a** and **3a′**. [b] Data for **3b** and **3b′**.

Another factor that influences the value of λ_{max} is the presence of an electron-donating alkyl group in **3b** and an electron-withdrawing cyano group in dyes **2**, **3a**, **4** and **5**.[24] After deprotonation and formation of the quinoidal structure, the negative charge that is delocalized on the imide structure acts as a donor and the arylimine group acts as an acceptor. The strong electron-withdrawing effect of the nitrile group led to an additional bathochromic shift of 46 nm and a higher extinction coefficient for **3a′** compared to **3b′** (Fig. 2 and Table 1).

Compound **3b**′ lost only 5% intensity in its absorption maximum after three days in a diluted acetone solution (ESI Fig. S5†). Repetitive titrations of **3b** in acetone with aqueous NaOH (0.1 M) and HCl (0.1 M) (five cycles), displayed the reversibility of the deprotonation (ESI Fig. S6†). This stability and reversibility ensures its potential application in NIR absorbing materials.[23]

In summary, a combined approach towards the NIR absorption of rylene dyes, based on core-extension, a push–pull effect and quinoidization, is presented. The amino-substituted perylene, terrylene and quaterrylene imides form a novel quinoidal charge delocalization system in the presence of base, which results in remarkable NIR absorptions at 826, 1008 and 1186 nm, respectively.

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Notes and references

1 P. Gregory, *High-Technology Applications of Organic Colorants*, Plenum Press, New York, 1991Z. Y. Wang, J. D. Zhang, X. G. Wu, M. Birau, G. Yu, H. G. Yu, Y. H. Qi, P. Desjardins, X. S. Meng, J. P. Gao, E. Todd, N. H. Song, Y. W. Bai, A. M. R. Beaudin and G. LeClair, *Pure Appl. Chem.*, 2004, **76**, 1435–1443; S. Wang, X. Z. Li, S. D. Xun, X. H. Wan and Z. H. Wang, *Macromolecules*, 2006, **39**, 7502–7507.

2 J. Fabian and R. Zahradník, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 677–694; J. Fabian, *Chem. Rev.*, 1992, **92**, 1197–1226.

3 H. Langhals, *Angew. Chem., Int. Ed.*, 2003, **42**, 4286–4288; M. Q. Tian, S. Tatsuura, M. Furuki, Y. Sato, I. Iwasa and L. S. Pu, *J. Am. Chem. Soc.*, 2003, **125**, 348–349; G. M. Fischer, A. P. Ehlers, A. Zumbusch and E. Daltrozzo, *Angew. Chem., Int. Ed.*, 2007, **46**, 3750–3753; K. Rurack, M. Kollmannsberger and J. Daub, *Angew. Chem., Int. Ed.*, 2001, **40**, 385–387; W. L. Zhao and E. M. Carreira, *Angew. Chem., Int. Ed.*, 2005, **44**, 1677–1679.

4 A. Tsuda and A. Osuka, *Science*, 2001, **293**, 79–82.

5 I. M. Blake, L. H. Ress, T. D. W. Claridge and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2000, **39**, 1818–1821.

6 S. Inoue, Y. Aso and T. Otsubo, *Chem. Commun.*, 1997, 1105–1106; T. Takahashi, K. Matsuoka, K. Takimiya, T. Otsubo and Y. Aso, *J. Am. Chem. Soc.*, 2005, **127**, 8928–8929.

7 M. Banerjee, S. V. Lindeman and R. Rathore, *J. Am. Chem. Soc.*, 2007, **129**, 8070–8071.

8 L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend and J. D. MacKenzie, *Science*, 2001, **293**, 1119–1122; M. A. Angadi, D. Cosztola and M. R. Wasielewski, *Mater. Sci. Eng., B*, 1999, **B63**, 191–194; L. Fan, Y. P. Xu and H. Tian, *Tetrahedron Lett.*, 2005, **46**, 4443–4447.

9 F. Holtrup, G. Müller, H. Quante, S. de Feyter, F. C. De Schryver and K. Müllen, *Chem.–Eur. J.*, 1997, **3**, 219–225; F. Nolde, J. Qu, C. Kohl, N. G. Pschirer, E. Reuther and K. Müllen, *Chem.–Eur. J.*, 2005, **11**, 3959–3967.

10 H. Quante and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1323–1325; Y. Geerts, H. Quante, H. Platz, R. Mahrt, M. Hopmeier, A. Böhm and K. Müllen, *J. Mater. Chem.*, 1998, **8**, 2357–2369; H. Langhals, J. Büttner and P. Blanke, *Synthesis*, 2005, 364–366.

11 N. G. Pschirer, C. Kohl, F. Nolde, J. Qu and K. Müllen, *Angew. Chem., Int. Ed.*, 2006, **45**, 1401–1404.

12 C. Kohl, S. Becker and K. Müllen, *Chem. Commun.*, 2002, 2278–2279.

13 Yu. Avlasevich and K. Müllen, *Chem. Commun.*, 2006, 4440–4442.

14 D. Gosztola, M. P. Niemczyk, W. S. Aaron, S. Lukas and M. R. Wasielewski, *J. Phys. Chem. A*, 2000, **104**, 6545–6551; M. J. Tauber, R. F. Kelley, J. M. Giaimo, B. Rybtchinski and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2006, **128**, 1782–1783.

15 N. G. Pschirer, J. Qu and M. Könemann, World Pat. WO/2006/117383, 2006.

16 Yu. Avlasevich and K. Müllen, *J. Org. Chem.*, 2007, **72**, 10243–10246.

17 T. Edvinsson, C. Li, N. G. Pschirer, J. Schöneboom, F. Eickemeyer, R. Sens, G. Boschloo, A. Herrmann, K. Müllen and A. Hagfeldt, *J. Phys. Chem. C*, 2007, **111**, 15137–15140.

18 S. Becker, A. Böhm and K. Müllen, *Chem.–Eur. J.*, 2000, **6**, 3984–3990.

19 According to Karplus theory,[20] for constant bond angles and hybridization, ^3J values will increase with an enhancement of the double bond character or a decrease in the double bond length. This rule has already been proven for the quinoidal terthiophene (^3J values of 4.5–5.4 Hz, compared with non-quinoidal 3.7–3.9 Hz)[21] and quinoidal tetraaminoperylene (9.6–9.8 and 8.1–8.5 Hz, correspondingly).[22].

20 M. Karplus, *J. Am. Chem. Soc.*, 1963, **85**, 2870–2871.

21 T. M. Pappenfus, J. D. Raff, E. J. Hukkanen, J. R. Burney, J. Casabo, S. M. Drew, L. L. Miller and K. R. Mann, *J. Org. Chem.*, 2002, **67**, 6015–6024.

22 L. H. Gade, C. H. Galka, K. W. Hellmann, R. M. Williams, L. D. Cola, I. J. Scowen and M. McPartlin, *Chem.–Eur. J.*, 2002, **8**, 3732–3746.

23 T. Gunnlaugsson, P. E. Kruger, P. Jensen, F. M. Pfeffer and G. M. Hussey, *Tetrahedron Lett.*, 2003, **44**, 8909–8913; B. Liu and H. Tian, *J. Mater. Chem.*, 2005, **15**, 2681–2686.

24 The electron-donating effect of the alkyl chain induced an additional red shift of 46 nm for **3b** compared to **3a**.