

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/228008295>

Design and Synthesis of a New Class of Photochromic Diarylethene-Containing Dithieno[3,2-b:2',3'-d]pyrroles and Their Switchable Luminescence Properties

ARTICLE *in* CHEMISTRY - A EUROPEAN JOURNAL · OCTOBER 2009

Impact Factor: 5.73 · DOI: 10.1002/chem.200900581 · Source: PubMed

CITATIONS

32

READS

17

5 AUTHORS, INCLUDING:



Chi-Chiu Ko

City University of Hong Kong

70 PUBLICATIONS 1,720 CITATIONS

SEE PROFILE



Nanyong Zhu

Hong Kong Baptist University

281 PUBLICATIONS 9,932 CITATIONS

SEE PROFILE



Vivian Wing-Wah Yam

The University of Hong Kong

483 PUBLICATIONS 16,813 CITATIONS

SEE PROFILE

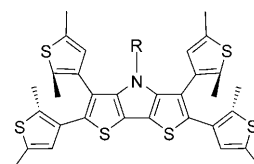
Design and Synthesis of a New Class of Photochromic Diarylethene-Containing Dithieno[3,2-b:2',3'-d]pyrroles and Their Switchable Luminescence Properties

Hok-Lai Wong,^[a] Chi-Chiu Ko,^[a, b] Wai Han Lam,^[a] Nianying Zhu,^[a] and Vivian Wing-Wah Yam^{*[a]}

Conjugated acenes and heteroacenes have received enormous attention in the past decade or so owing to their probable applications in the fabrication of high-performance semiconductor devices.^[1] Amongst them, dithieno[3,2-b:2',3'-d]pyrroles represent one class of interesting compounds that can function as efficient fluorescent materials,^[2] low-band-gap field-effect transistors, and organic semiconductors.^[3] In addition, the recent interest in the development of nondoped organic light-emitting diodes (OLEDs), which often requires bipolar design to facilitate exciton formation,^[4a-e] has led to the exploration of common electron donors such as triarylamine and carbazole.^[4f-m] Being an analogue of carbazole, dithienopyrrole derivatives have also been explored for use as a new class of bipolar materials in high efficiency OLEDs.^[4n]

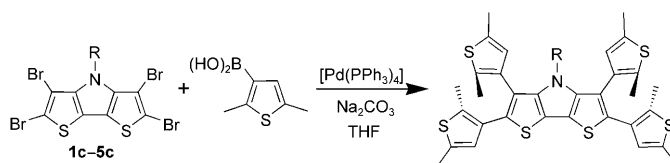
On the other hand, photochromic diarylethenes also possess excellent and promising switching properties,^[5] with high fatigue resistance, high stability, and fast response time. Our group has recently directed our interests in functionalizing materials with diarylethenes and studying their photochromic behavior.^[6] With our recent experience in working on photochromic fused-thiophene systems,^[6f] we have ex-

tended our interest towards the functionalization of dithieno[3,2-b:2',3'-d]pyrroles owing to their desirable semiconducting properties and their ease of functionalization at the pyrrole ring. Introduction of an optically addressable switching unit into dithieno[3,2-b:2',3'-d]pyrrole system may give rise to new classes of interesting materials with photoswitchable luminescence and electronic properties. Herein are described the synthesis and the photophysical study of a new class of photochromic dithieno[3,2-b:2',3'-d]pyrrole derivatives **1–5**.



- 1 R = C₆H₅
- 2 R = C₆H₄CH₃-*p*
- 3 R = C₆H₄OCH₃-*p*
- 4 R = C₆H₄Cl-*p*
- 5 R = *n*-C₄H₉

Of the different methods employed in synthesizing the dithieno[3,2-b:2',3'-d]pyrrole core,^[7] the synthetic methodology developed by Rasmussen and co-workers^[7a,e] was adopted. Tetrabromination of dithieno[3,2-b:2',3'-d]pyrrole followed by subsequent Suzuki cross-coupling reaction in the presence of an excess of 2,5-dimethylthien-3-yl boronic acid, aqueous Na₂CO₃ and a catalytic amount of [Pd(PPh₃)₄] in THF under reflux conditions (Scheme 1) afforded the desired compounds in moderate yield.



Scheme 1. Synthetic route for **1–5**.

[a] H.-L. Wong, Dr. C.-C. Ko, Dr. W. H. Lam, Dr. N. Zhu, Prof. Dr. V. W.-W. Yam
Centre for Carbon-Rich Molecular and Nano-Scale Metal-Based Materials Research
Department of Chemistry and HKU-CAS Joint Laboratory of New Materials
The University of Hong Kong, Pokfulam Road
Hong Kong (P.R. China)
Fax: (+852)2857-1586
E-mail: wwyam@hku.hk

[b] Dr. C.-C. Ko
Present address: Department of Biology and Chemistry
City University of Hong Kong
Tat Chee Avenue, Kowloon, Hong Kong (P.R. China)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200900581>.

Compounds **1–5** have been characterized by ^1H NMR spectroscopy, EI-MS, and give satisfactory elemental analyses, while the structures of compound **2** and **3** have been determined by X-ray crystallography. A representative perspective drawing of **2** is depicted in Figure 1. The *N*-aryl

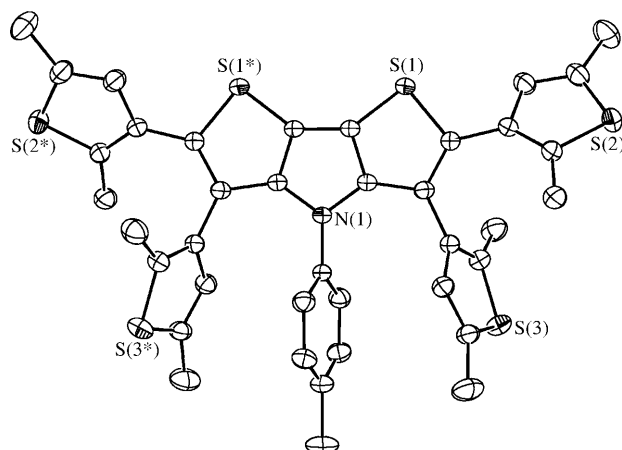


Figure 1. Perspective drawing of **2**. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are shown at the 30% probability level.

plane is twisted from the dithienopyrrole core by about 74° for **2** and 66° for **3**. The diarylethene groups in **2** are both in an anti-parallel configuration, while only one of them is found to be in an anti-parallel configuration in **3**, as shown in Figure S1 in the Supporting Information.

Compounds **1–5** dissolve in benzene and they showed similar UV/Vis absorption spectra with an intense band at about 350 nm. An additional shoulder at approximately 325 nm was observed for **1–4**. The intense band at 350 nm is ascribed to the $\pi \rightarrow \pi^*$ transitions of the dithienopyrrole core mixed with the dimethylthiophene moieties, while the shoulder at 325 nm that could only be found in **1–4** may be attributed to the $\pi \rightarrow \pi^*$ transition resulting from the presence of the *N*-aryl rings. The relative insensitivity of the absorption energies of the 350 nm band to the nature of the *N*-substituent is suggestive of the non-coplanarity of the *N*-aryl ring to the plane of the dithienopyrrole core, as similarly observed in the X-ray crystal structures of **2** and **3**. Upon excitation at the transition band at 360 nm in degassed benzene, the solutions of compound **1–5** showed photochromic behavior, turning from colorless to reddish purple, with the growth of an intense absorption band at approximately

370 nm and a broad absorption at about 558 nm in the UV/Vis spectra (Figure 2), typical of the absorptions of the closed form.^[5,6] Two well-defined isosbestic points at about

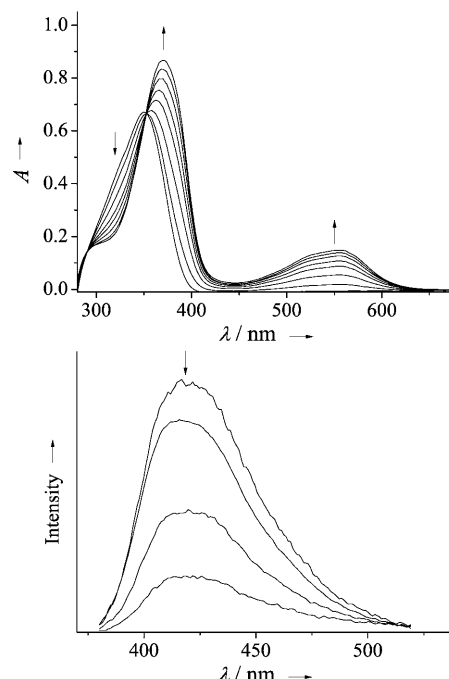
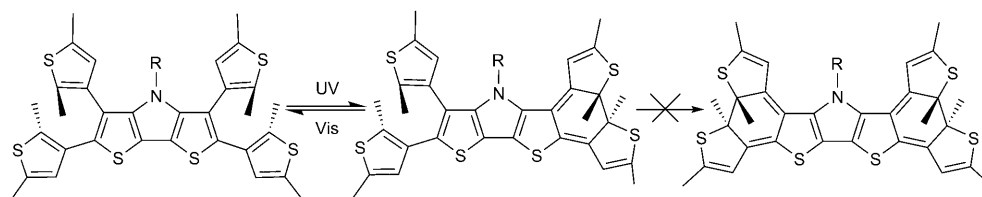


Figure 2. UV/Vis absorption spectral changes of **5** (1.92×10^{-5} M) upon irradiation at 360 nm (top) and its fluorescence spectral changes ($\lambda_{\text{exc}} = 352$ nm) in degassed benzene (bottom).

290 and 352 nm were observed, suggesting the photocyclization of only a pair of diarylethene units, probably due to the effective energy transfer from the dithienylethene moiety to the 8a,8b-dimethyl-1,8-dithia-*as*-indacene moiety (closed form) after the first cyclization,^[6f,8] as illustrated in Scheme 2. Further prolongation of irradiation did not produce the double photocyclized product. Upon excitation at the absorption band of the closed form at 470–600 nm, the UV/Vis absorption spectral changes were reversed, resulting from the regeneration of the open form. The cyclo-reversibility has been demonstrated in **4** with at least three repeating cycles (Figure S2 in the Supporting Information).

On excitation into the $\pi \rightarrow \pi^*$ absorption band ($\lambda \leq 400$ nm) of **1–5**, intense blue fluorescence with lifetimes of less than one nanosecond was observed. The photophysical



Scheme 2. Photochromic reactions for **1–5**.

Table 1. Photophysical data of **1–5** in benzene at 298 K.

		Absorption λ_{abs} [nm] (ϵ [dm ³ mol ⁻¹ cm ⁻¹])	Emission λ_{em} [nm] (Φ_{lum})
1	open	326 sh (18360), 348 (23300)	417 (0.14)
	closed	370 sh (31830), 380 (32860), 532 sh (7330), 558 (8070)	–
2	open	325 sh (20240), 349 (26720)	410 (0.16)
	closed	368 sh (33700), 380 (35010), 532 sh (7210), 558 (7930)	–
3	open	326 sh (19940), 349 (25250)	418 (0.13)
	closed	370 sh (33870), 380 (34870), 530 sh (7510), 558 (8420)	–
4	open	324 sh (15230), 349 (19840)	422 (0.14)
	closed	368 sh (31730), 382 (37120), 528 sh (7930), 558 (8940)	–
5	open	350 (35590)	417 (0.18)
	closed	298 (8160), 372 (49450), 528 sh (8310), 556 (9300)	–

data are summarized in Table 1. Photocyclization of all the compounds resulted in a reduced fluorescence intensity (Figure 2). This is probably due to the existence of lower lying excited states of the closed form, which would quench the emission and inactivate the second photocyclization step. The photochromic quantum yields have also been measured (Table 2). The photocyclization quantum yield^[9] is found to be much higher than that for photocycloreversion, which is typical of the diarylethene systems.^[5,6] Half-lives of the closed form of compound **4** have also been investigated at 298 and 328 K (Table S4 in the Supporting Information).

All of the compounds exhibit a quasi-reversible oxidation couple and two irreversible oxidative waves at higher potentials (Table 3). No reduction wave was observed upon scanning up to -2.5 V. The first oxidation couple is probably due to the formation of the cation radical in the dithienopyrrole core. This assignment is further supported by the sensitivity of the oxidation potential to the change of N-substituents on the dithienopyrrole. In light of the absence of the second and the third oxidation wave in the unsubstituted

(**2b**) and tetrabrominated dithienopyrroles (**2c**) as well as the relative insensitivity of these oxidation potentials to the change of the N-substituent, the irreversible oxidation waves at higher oxidation potentials are likely attributed to the oxidations of the peripheral dimethylthiophene units.

To gain a deeper insight into the nature of the electronic absorption and emission properties of this class of compounds,

calculations using DFT, TDDFT, HF, and CIS methods were performed for the open and closed forms of **1–5**.^[10]

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for the PBE0 optimized structure of the open forms of **1–5** are mainly contributed from the respective π and π^* orbitals of the dithienopyrrole core, mixed slightly with the π and π^* orbitals of the peripheral thiophene rings. However, the HOMO and LUMO for the PBE0 optimized structure of closed forms of **1–5** are the π and π^* orbitals localized on the condensed thiophene moiety, respectively. Figure 3 shows the spatial plots of selected frontier molecular orbitals of the two forms of **1**. A HOMO–LUMO energy gap of the open forms is in the range of 4.20–4.24 eV (Table S6 in the Supporting Information), while a significant decrease in energy gap is found in the closed forms (2.63–2.71 eV) as a more extended π conjugation in the condensed thiophene moiety leads to the increase in energy of π and decrease in energy of π^* orbitals.

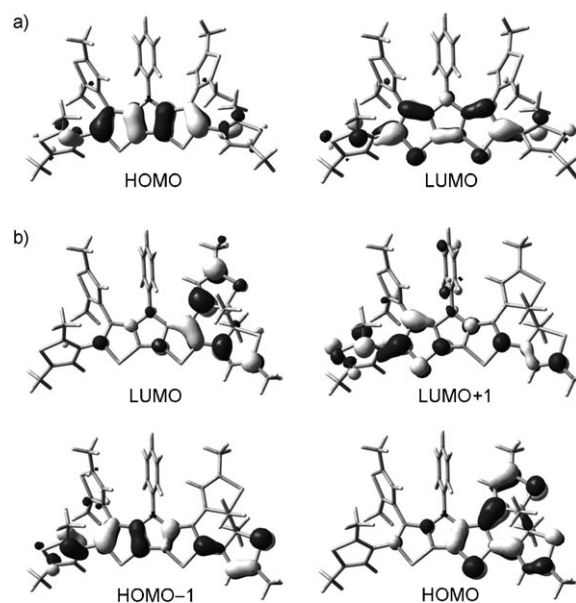
Table 2. Photochemical quantum yields of **1–5** in degassed benzene solution at 293 K.

	Photocyclization, Φ_{350}	Photocycloreversion, Φ_{500}
1	0.37	0.11
2	0.38	0.10
3	0.37	0.08
4	0.35	0.11
5	0.38	0.09

Table 3. Electrochemical data of **1–5** in THF.^[a]

	$E_{1/2}$ [V]	ΔE_p [mV]	E_{pa} [V]
1	+0.78	89	+1.03, +1.42
2	+0.77	95	+1.03, +1.41
3	+0.75	91	+1.03, +1.50
4	+0.80	101	+1.03, +1.44
5	+0.74	95	+1.03, +1.41
2b	–	–	+1.10
2c	–	–	+1.27

[a] All potentials are versus SCE. Data were recorded under argon with 0.10 M *n*Bu₄NPF₆ as the supporting electrolyte. $E_{1/2}$ is $(E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively. E_p is the peak-to-peak separation.

Figure 3. Spatial plots (isovalue = 0.04) of selected TDDFT/CPCM frontier molecular orbitals of the open form (a) and closed form (b) in **1**.

Selected singlet–singlet transitions of the open and closed forms in **1–5** are listed in Table S7 and Table S8, respectively, in the Supporting Information. The spectral assignment is based on the correlation of the experimental band maxima with the calculated excitation wavelengths of the transitions with significant oscillator strengths. The absorption bands of the open form are computed at 343–347 nm for **1–5**. This transition mainly corresponds to an excitation from HOMO to LUMO, which can be assigned as the $\pi \rightarrow \pi^*$ transition of the dithienopyrrole core, slightly mixed with the $\pi \rightarrow \pi^*$ transition of the peripheral thiophene rings. These calculated wavelengths are in excellent agreement with the λ_{max} in the major electronic absorption bands of the open forms.

For the closed forms in **1–5**, the low-energy absorption band corresponds to the transition to the first singlet excited state (S_1) computed at 578–595 nm, which is mainly consisted of an excitation from HOMO to LUMO, and can be assigned as the $\pi \rightarrow \pi^*$ transition of the condensed thiophene moiety. The most intense transition with the calculated excitation wavelengths (377–389 nm) compares well with the λ_{max} in the high-energy absorption band observed in the electronic absorption spectra. For compounds **1–3** and **5**, the transition is mainly composed of a combination of two excitations HOMO–1 \rightarrow LUMO and HOMO \rightarrow LUMO+1. As shown in Figure 3, the HOMO–1 and LUMO+1 are π and π^* orbitals concentrated on the dithienopyrrole core and the peripheral thiophenes, respectively. In view of the topologies of the MOs involved in the transition, the high-energy absorption band can be assigned as the $\pi \rightarrow \pi^*$ transition with charge transfer character. In addition to the HOMO–1 \rightarrow LUMO excitation, the most intense transition at 381 nm for **4** is composed of HOMO \rightarrow LUMO+2 and HOMO \rightarrow LUMO+3 excitations, in which the LUMO+2 and LUMO+3 can be considered as the π^* orbitals of the dithienopyrrole core and the peripheral thiophenes, but with a significant contribution from the *N*-aryl ring.

The first singlet excited state of the open forms in **1–5** was optimized using the CIS method. On the basis of these S_1 optimized geometries, the lowest energy transition is computed at 393–394 nm using the TDDFT/CPCM method at the PBE0 level and consisted of $\pi \rightarrow \pi^*$ transition of the dithienopyrrole core (Table S9 in the Supporting Information). The major geometrical changes in the excited states relative to the corresponding ground states occur mainly in the dithienopyrrole core, in which the C=C bonds are lengthened whereas the C–C bonds are shortened (Table S10 in the Supporting Information). The feature is understandable, as the excited state involves population of the LUMO which contains quinoid character.

In conclusion, a series of dithienylethene-containing dithieno[3,2-b:2',3'-d]pyrroles has been synthesized. Photo-physical, photochromic, electrochemical, and computational studies have been carried out. The crystal structures of **2** and **3** have been determined. Further investigations on their possible applications are in progress.

Experimental Section

Details of the syntheses and characterization of compounds **1–5** can be found in the Supporting Information. CCDC-722353 (**2**) and 722352 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

V.W.-W.Y. acknowledges support from The University of Hong Kong under the Distinguished Research Achievement Award Scheme, the University Development Fund, the Faculty Development Fund, and the URC Strategic Research Theme on Molecular Materials. This work has been supported by a GRF Grant (Project No. HKU7057/07P) and a CAV Grant (Project No. HKU2/05C) from the Research Grants Council of Hong Kong Special Administrative Region (P.R. China). H.-L.W. acknowledges the receipt of a postgraduate studentship and W.H.L. the receipt of a University Postdoctoral Fellowship, both from The University of Hong Kong. We also thank the Computer Center at The University of Hong Kong for providing the computational resources.

Keywords: density functional calculations • luminescence • materials • nitrogen heterocycles • photochromism • sulfur heterocycles

- [1] a) J. Roncali, *Chem. Rev.* **1992**, 92, 711–738; b) X.-C. Li, H. Sirringhaus, F. Garnier, A. B. Holmes, S. C. Moratti, N. Feeder, W. Clegg, S. J. Teat, R. H. Friend, *J. Am. Chem. Soc.* **1998**, 120, 2206–2207.
- [2] K. R. Radke, K. Ogawa, S. C. Rasmussen, *Org. Lett.* **2005**, 7, 5253–5256.
- [3] a) J. Liu, R. Zhang, G. Sauvé, T. Kowalewski, R. D. McCullough, *J. Am. Chem. Soc.* **2008**, 130, 13167–13176; b) T. M. Pappenfus, B. J. Hermanson, T. J. Helland, G. G. W. Lee, S. M. Drew, K. R. Mann, K. A. McGee, S. C. Rasmussen, *Org. Lett.* **2008**, 10, 1553–1556; c) W. Zhang, J. Li, L. Zou, B. Zhang, J. Qin, Z. Lu, Y. F. Poon, M. B. Chan-Park, C. M. Li, *Macromolecules* **2008**, 41, 8953–8955; d) E. Zhou, M. Nakamura, T. Nishizawa, Y. Zhang, Q. Wei, K. Tajima, C. Yang, K. Hashimoto, *Macromolecules* **2008**, 41, 8302–8305; e) K. Ogawa, J. A. Stafford, S. D. Rothstein, D. E. Tallman, S. C. Rasmussen, *Synth. Met.* **2005**, 152, 137–140.
- [4] a) S.-L. Lin, L.-H. Chan, R.-H. Lee, M.-Y. Yen, W.-J. Kuo, C.-T. Chen, R.-J. Jeng, *Adv. Mater.* **2008**, 20, 3947–3952; b) Y. Shirota, M. Kinoshita, T. Noda, K. Okumoto, T. Ohara, *J. Am. Chem. Soc.* **2000**, 122, 11021–11022; c) H. Doi, M. Kinoshita, K. Okumoto, Y. Shirota, *Chem. Mater.* **2003**, 15, 1080–1089; d) T.-H. Huang, J. T. Lin, L.-Y. Chen, Y.-T. Lin, C.-C. Wu, *Adv. Mater.* **2006**, 18, 602–606; e) A. P. Kulkarni, X. Kong, S. A. Jenekhe, *Adv. Funct. Mater.* **2006**, 16, 1057–1066; f) Z. Liu, Z. Bian, L. Ming, F. Ding, H. Shen, D. Nie, C. Huang, *Org. Electron.* **2008**, 9, 171–182; g) S. Tang, M. Liu, P. Lu, H. Xia, M. Li, Z. Xie, F. Shen, C. Gu, H. Wang, B. Yang, Y. Ma, *Adv. Funct. Mater.* **2007**, 17, 2869–2877; h) W.-Y. Wong, C.-L. Ho, Z.-Q. Gao, B.-X. Mi, C.-H. Chen, K.-W. Cheah, Z. Lin, *Angew. Chem.* **2006**, 118, 7964–7967; *Angew. Chem. Int. Ed.* **2006**, 45, 7800–7803; i) Z. Liu, M. Guan, Z. Bian, D. Nie, Z. Gong, Z. Li, C. Huang, *Adv. Funct. Mater.* **2006**, 16, 1441–1448; j) A. van Dijken, J. J. A. M. Bastiaansen, N. M. M. Kiggen, B. M. W. Langeveld, C. Rothe, A. Monkman, I. Bach, P. Stössel, K. Brunner, *J. Am. Chem. Soc.* **2004**, 126, 7718–7727; k) O. Kwon, S. Barlow, S. A. Odom, L. Beverina, N. J. Thompson, E. Zojer, J.-L. Brédas, S. R. Marder, *J. Phys. Chem. A* **2005**, 109, 9346–9352; l) Z. Ge, T. Hayakawa, S. Ando, M. Ueda, T. Akiike, H. Miyamoto, T. Kajita, M.-a. Kakimoto, *Adv. Funct. Mater.* **2008**, 18, 584–590; m) J. M. Hancock, A. P. Gifford, Y. Zhu,

- Y. Lou, S. A. Jenekhe, *Chem. Mater.* **2006**, *18*, 4924–4932; n) T. T. Steckler, X. Zhang, J. Hwang, R. Honeyager, S. Ohira, X.-H. Zhang, A. Grant, S. Ellinger, S. A. Odom, D. Sweat, D. B. Tanner, A. G. Rinzier, S. Barlow, J.-L. Brédas, B. Kippelen, S. R. Marder, J. R. Reynolds, *J. Am. Chem. Soc.* **2009**, *131*, 2824–2826.
- [5] a) M. Irie, K. Uchida, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 985–996; b) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716; c) K. Matsuda, M. Irie, *J. Photochem. Photobiol. C* **2004**, *5*, 169–182; d) H. Tian S. Yang, *Chem. Soc. Rev.* **2004**, *33*, 85–97; e) Y. Feng, Y. Yan, S. Wang, W. Zhu, S. Qian, H. Tian, *J. Mater. Chem.* **2006**, *16*, 3685–3692; f) X. Li, H. Tian, *Tetrahedron Lett.* **2005**, *46*, 5409–5412; g) H. D. Samachetty, V. Lemieux, N. R. Branda, *Tetrahedron* **2008**, *64*, 8292–8300; h) F. M. Raymo, M. Tomasulo, *Chem. Soc. Rev.* **2005**, *34*, 327–336; i) P. Belser, L. De Cola, F. Hartl, V. Adamo, B. Bozic, Y. Chriqui, V. M. Iyer, R. T. F. Jukes, J. Kühni, M. Querol, S. Roma, N. Salluce, *Adv. Funct. Mater.* **2006**, *16*, 195–208.
- [6] a) V. W.-W. Yam, C.-C. Ko, N. Zhu, *J. Am. Chem. Soc.* **2004**, *126*, 12734–12735; b) C.-C. Ko, W.-M. Kwok, V. W.-W. Yam, D. L. Phillips, *Chem. Eur. J.* **2006**, *12*, 5840–5848; c) T.-W. Ngan, C.-C. Ko, N. Zhu, V. W.-W. Yam, *Inorg. Chem.* **2007**, *46*, 1144–1152; d) J. K.-W. Lee, C.-C. Ko, K. M.-C. Wong, N. Zhu, V. W.-W. Yam, *Organometallics* **2007**, *26*, 12–15; e) P. H.-M. Lee, C.-C. Ko, N. Zhu, V. W.-W. Yam, *J. Am. Chem. Soc.* **2007**, *129*, 6058–6059; f) C.-C. Ko, W. H. Lam, V. W.-W. Yam, *Chem. Commun.* **2008**, 5203–5205.
- [7] a) K. Ogawa, S. C. Rasmussen, *J. Org. Chem.* **2003**, *68*, 2921–2928; b) G. Koeckelberghs, L. De Cremer, W. Vanormelingen, W. Dehaen, T. Verbiest, A. Persoons, C. Samyn, *Tetrahedron* **2005**, *61*, 687–691; c) S. A. Odom, K. Lancaster, L. Beverina, K. M. Lefler, N. J. Thompson, V. Coropceanu, J.-L. Brédas, S. R. Marder, S. Barlow, *Chem. Eur. J.* **2007**, *13*, 9637–9646; d) P. Zanirato, P. Spagnolo, G. Zanardi, *J. Chem. Soc. Perkin Trans. 1* **1983**, 2551–2554; e) K. Ogawa, K. R. Radke, S. D. Rothstein, S. C. Rasmussen, *J. Org. Chem.* **2001**, *66*, 9067–9070.
- [8] a) K. Yagi, M. Irie, *Chem. Lett.* **2003**, *32*, 848–849; b) A. Peters, N. R. Branda, *Adv. Mater. Opt. Electron.* **2000**, *10*, 245–249; c) T. Kaieda, S. Kobatake, H. Miyasaka, M. Murakami, N. Iwai, Y. Nagata, A. Itaya, M. Irie, *J. Am. Chem. Soc.* **2002**, *124*, 2015–2024; d) K. Higashiguchi, K. Matsuda, M. Matsuo, T. Yamada, M. Irie, *J. Photochem. Photobiol. A* **2002**, *152*, 141–146; e) K. Higashiguchi, K. Matsuda, M. Irie, *Angew. Chem.* **2003**, *115*, 3661–3664; *Angew. Chem. Int. Ed.* **2003**, *42*, 3537–3540; f) K. Higashiguchi, K. Matsuda, N. Tanifuji, M. Irie, *J. Am. Chem. Soc.* **2005**, *127*, 8922–8923.
- [9] The quantum yields have not been corrected to the active anti-parallel conformation as the two forms are readily inter-converted and are in dynamic equilibrium at room temperature.
- [10] See the Supporting Information for the computational details.

Received: March 4, 2009

Published online: August 19, 2009