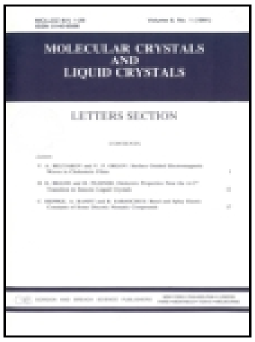

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Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Che-Wei Chang & Kew-Yu Chen (2016) Crystal structure of N,N '-bis(cyclohexyl)-1-(N,N-dihexylamino)perylene-3,4:9,10-bis(dicarboximide), Molecular Crystals and Liquid Crystals, 624:1, 205-212, DOI: 10.1080/15421406.2015.1036501

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1036501

MOL. CRYST. LIQ. CRYST.
2016, VOL. 624, NO. 1, 205–212
http://dx.doi.org/10.1080/15421406.2015.1036501

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Crystal structure of *N,N′*-bis(cyclohexyl)-1-(*N,N*-dihexylamino)perylene-3,4:9,10-bis(dicarboximide)

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ABSTRACT
An asymmetric dialkylamino-substituted perylene bisimide (**1**), N,N′-bis (cyclohexyl)-1-(N,N-dihexylamino)perylene-3,4:9,10-bis(dicarboximide), was synthesized and characterized by single-crystal X-ray diffraction. The crystal belongs to triclinic, space group P–1, with a = 9.8924(6), b = 14.6338(10), c = 15.6221(10) Å, α= 105.098(3)°, β = 103.386(2)°, γ = 107.772(3)°, and Z = 2. The central perylene core of **1** is twisted with dihedral angles of 14.9(3)° and 11.6(3)°; this twist configuration induces the axial chirality in this family of perylene bisimide dyes. In the crystal structure, the intermolecular C–H···O interaction links a pair of molecules into a cyclic centrosymmetric dimer that is connected to one another via the intermolecular π–π stacking, so linking the molecules into a continuous one-dimensional framework along the [100] direction.

KEYWORDS
Axial chirality; enantiomer; perylene bisimides; perylene dianhydrides; x-ray diffraction

Introduction

Perylene bisimide (PBI) and its derivatives have received significant attention due to their potential applications in molecular optoelectronic devices, such as organic field-effect transistors (OFETs) [1, 2], light-emitting diodes [3, 4], photovoltaic cells [5, 6], light-harvesting arrays [7, 8], photochromic materials [9, 10], and LCD color filters [11, 12]. This family of organic dyes is advantageous due to their high molar absorptivities, excellent thermal, and optical stabilities, high photoluminescence quantum yields, reversible redox properties, ease of synthetic modification, and self-assembly behaviors [13–15]. The electronic characteristics of PBIs can also be fine-tuned by the substitution of the conjugated perylene core. Based on these principles, many PBI derivatives with either electron-withdrawing or electron-donating groups have been designed and synthesized [16–25] In an effort to expand the scope of PBI-based chromophores available for designing systems for green dyes and charge transport, we synthesized a monosubstituted perylene bisimide derivative (**1**), *N,N′*-bis(cyclohexyl)-1-(*N,N*-dihexylamino)perylene-3,4:9,10-bis(dicarboximide) [26]. Herein, we report the X-ray structure of **1**, and compare it with those of disubstituted and tetrasubstituted PBIs. The results offer the potential to synthesize PBI derivatives with extended molecular architectures and photophysical properties.

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Experimental

Chemicals and instruments

The starting materials, such as 3,4,9,10-perylenetetracarboxylic dianhydride, cyclohexylamine, acetic acid, *N*-methyl-2-pyrrolidinone (NMP), cerium (IV) ammonium nitrate (CAN), tin (II) chloride dihydrate ($SnCl_2.2H_2O$), tetrahydrofuran (THF), sodium hydride (NaH), and 1-iodohexane ($C_6H_{13}I$) were purchased from Merck, ACROS and Sigma–Aldrich. Column chromatography was performed using silica gel Merck Kieselgel *si* 60 (40–63 mesh).

^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker 400 MHz NMR spectrometer. Mass spectra were recorded on a VG70-250S mass spectrometer. The single-crystal X-ray diffraction data were collected on a Bruker Smart 1000CCD area-detector diffractometer.

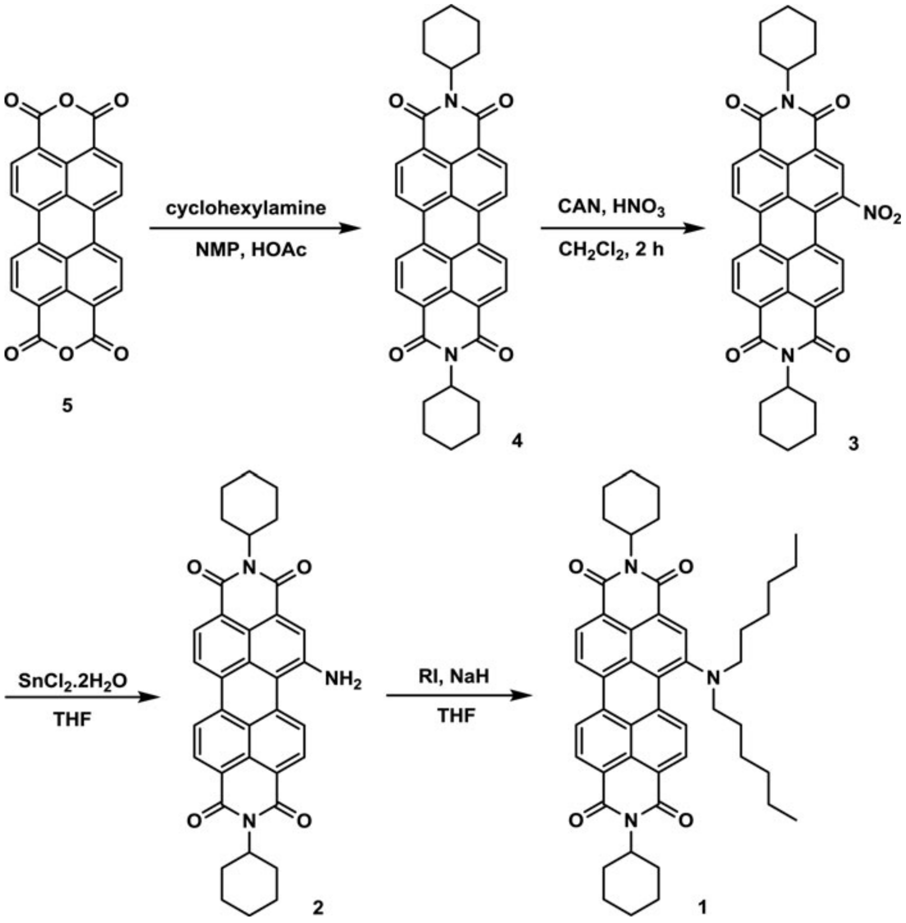
Synthesis and characterization

Synthesis of 1

A mixture of a solution of **2** (400 mg, 0.70 mmol), sodium hydride (97%, 100 mg, 4.00 mmol) and dry THF (50 mL) was stirred at 0°C under N_2 for 30 min. 1-Iodohexane (1.60 mmol) was then added, and the resulting mixture was stirred for 2 h. The resulting mixture was diluted with 15 mL of water and extracted with CH_2Cl_2. The crude product was purified by silica gel column chromatography with eluent ethyl acetate/*n*-hexane (1/2) to afford **1** in an 85% yield. Characterization data for **1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (d, $J = 8.0$ Hz, 1H), 8.49–8.53 (m, 2H), 8.48 (s, 1H), 8.31–8.39 (m, 3H), 5.02 (m, 2H), 3.40 (m, 2H), 3.06 (m, 2H), 2.55 (m, 4H), 1.90 (m, 4H), 1.62–1.79 (m, 8H), 1.46 (m, 4H), 1.16–1.30 (m, 16H), 0.77 (t, $J = 6.4$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.07, 164.06, 163.99, 163.86, 150.56, 135.47, 134.63, 133.53, 131.41, 130.61, 129.11, 128.95, 128.10, 126.98, 126.94, 126.93, 124.80, 124.03, 123.44, 123.19, 122.76, 122.11, 121.30, 121.19, 54.04, 53.82, 52.55, 31.44, 29.67, 29.18, 29.11, 27.47, 26.89, 26.59, 25.51, 22.52, 13.89; MS (FAB): m/z (relative intensity) 738 ($M + H^+$, 100); HRMS: calculated for $C_{48}H_{56}O_4N_3$ 738.4271, found 738.4277. Green parallelepiped-shaped crystals suitable for the crystallographic studies reported here were isolated over a period of six weeks by slow evaporation from a dichloromethane solution.

Crystal structural determination

A single crystal of **1** with dimensions of 0.48 mm × 0.12 mm × 0.03 mm was selected. The lattice constants and diffraction intensities were measured with a Bruker Smart 1000 CCD area detector radiation ($\lambda = 0.71073$ Å) at 150(2) K. An ω-2θ scan mode was used for data collection in the range of $2.22 \leq \theta \leq 26.507$. A total of 32126 reflections were collected and 8084 were independent ($R_{\text{int}} = 0.0626$), of which 4733 were considered to be observed with $I > 2\sigma(I)$ and used in the succeeding refinement. The structure was solved by direct methods with SHELXS-97 [27] and refined on F^2 by full-matrix least-squares procedure with Bruker SHELXL-97 packing [28]. All nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms refined with riding model position parameters isotropically were located from difference Fourier map and added theoretically. At the final cycle of refinement, $R = 0.0644$ and $wR = 0.1601$ ($w = 1/[\sigma^2(F_o{}^2) + (0.0871P)^2 + 0.8402P]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$), $S = 1.047$, $(\Delta/\sigma)_{\max} = 0.001$, $(\Delta/\rho)_{\max} = 0.337$ and $(\Delta/\rho)_{\min} = -0.375$ e/Å^3.



Scheme 1. The synthetic route and the structure for **1**.

Results and discussion

The synthetic route and the structure for 1

Scheme 1 depicts the chemical structure and the synthetic route of **1**. In brief, the synthesis of **1** started from an imidization of 3,4,9,10-perylenetetracarboxylic dianhydride (**5**) and cyclohexylamine, followed by the mono-nitration of perylene bisimide (**4**), giving a nitro compound **3**. Next, the reduction of 1-nitroperylene bisimide (**3**) by tin (II) chloride dihydrate ($SnCl_2{\cdot}2H_2O$) gave 1-aminoperylene bisimide (**2**). Finally, an asymmetric dialkylamino-substituted perylene bisimide (**1**) was synthesized by the alkylation of **2** with 1-iodohexane. To confirm its structure, a single crystal of **1** was obtained from a dichloromethane solution, and the molecular structure was determined by X-ray diffraction analysis.

Figure 1 shows the ORTEP (Oak Ridge Thermal Ellipsoid Plot) diagram of **1** and the numbering of the atoms. Compound **1** crystallizes in the triclinic space group *P*–1, with $a = 9.8924(6)$, $b = 14.6338(10)$, $c = 15.6221(10)$ Å, $\alpha = 105.098(3)°$, $\beta = 103.386(2)°$, $\gamma = 107.772(3)°$, and $Z = 2$ (Table 1). The central perylene core of **1** is twisted with dihedral angles of 14.9(3)° and 11.6(3)° associated with bay area carbon atoms C11–C10–C13–C22 and C7–C8–C15–C16, respectively, these values being smaller than those of disubstituted and tetrasubstituted PBIs [14, 29, 30]. This twist configuration also induces the axial chirality in this

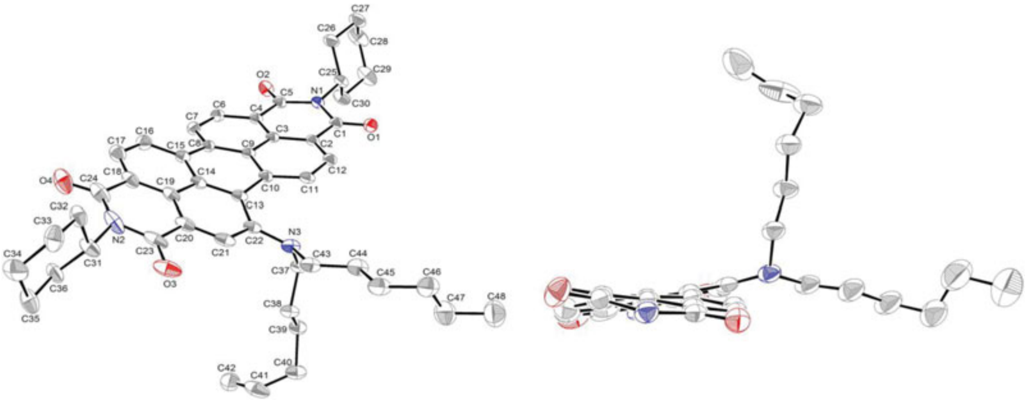


Figure 1. Molecular structure of **1** (left) and view along the N–N axis showing the twisted perylene backbone (right, alkyl groups at imide nitrogen atoms and all hydrogen atoms are omitted for clarity). Displacement ellipsoids are drawn at the 50% probability level.

Table 1. Crystallographic data for compound **1**.

Compound	**1**
Chemical formula	$C_{48}H_{55}N_3O_4$
Formula weight	737.95
Crystal system	Triclinic
Space group	*P*–1
a (Å)	9.8924(6)
b (Å)	14.6338(10)
c (Å)	15.6221(10)
α (°)	105.098(3)
β (°)	103.386(2)
γ (°)	107.772(3)
Volume (Å^3)	1956.7(2)
Z	2
D_{calc} (g cm^{-3})	1.253
μ (mm^{-1})	0.079
F_{000}	792
Crystal size (mm^3)	0.48 × 0.12 × 0.03
θ range (°)	2.22–26.50
Index ranges	$-12 \leqq h \leqq 12$ $-18 \leqq k \leqq 18$ $-19 \leqq l \leqq 19$
Reflections collected	32126
Independent reflections (R_{int})	8084 (0.0626)
Refinement method on F^2	Full-matrix least-squares
GOF on F^2	1.047
R_1 [$I > 2\sigma(I)$]	0.0644
wR_2 [$I > 2\sigma(I)$]	0.1601
R_1 (all data)	0.1208
wR_2 (all data)	0.2001
Residual (e Å^{-3})	0.337 and –0.375

family of PBI dyes. As shown in Fig. 2, there are two molecules with opposite chirality in the unit cell. However, the enantiomers are only observed in the crystalline state due to the low barrier of rotation in solution. Moreover, all C–C bond lengths of the perylene scaffold range between 1.358 and 1.486 Å (Table 2), which demonstrates the presence of π-conjugation for all C–C bonds. The longest bonds in the perylene moiety are the C8–C15 and C10–C13 bonds that connect the two naphthalene rings at a distance of 1.47 Å. The bond length is nearly identical to the lengths observed for other PBIs [14,29,30]. The results indicate that the degree of

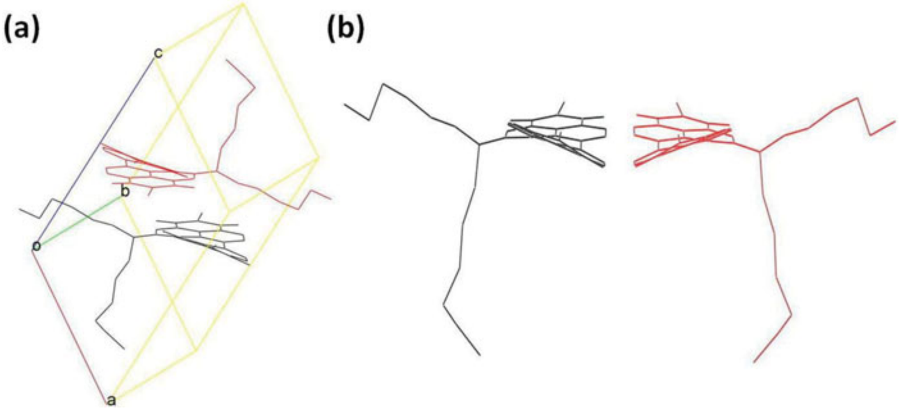


Figure 2. (a) Crystal structure of **1** in the unit cell. (b) The black-colored molecule is the *M* enantiomer and the red-colored one is the *P* enantiomer. For clarity, only the PBI scaffold and the alkyl amino groups are shown.

Table 2. Geometric parameters of **1** (Å and °).

Bond lengths (Å)	
C(1)–O(1)	1.220 (3)
C(1)–N(1)	1.403 (3)
C(1)–C(2)	1.469 (3)
C(3)–C(4)	1.414 (3)
C(6)–C(7)	1.388 (3)
C(8)–C(9)	1.414 (3)
C(8)–C(15)	1.464 (3)
C(10)–C(13)	1.475 (3)
C(14)–C(19)	1.427 (3)
C(20)–C(21)	1.358 (4)
C(20)–C(23)	1.486 (4)
Bond angles (°)	–
O(1)–C(1)–C(2)	122.0 (2)
C(2)–C(3)–C(4)	119.3 (2)
C(11)–C(10)–C(13)	123.4 (2)
C(13)–C(14)–C(19)	120.6 (2)
C(23)–N(2)–C(24)	123.8 (3)
C(22)–N(3)–C(37)	116.8 (2)
Torsion angles (°)	–
C(7)–C(8)–C(15)–C(16)	11.6 (3)
C(11)–C(10)–C(13)–C(22)	14.9 (3)
O(1)–C(1)–C(2)–C(12)	3.4 (4)
C(19)–C(14)–C(15)–C(16)	3.0 (4)

conjugation of the perylene backbone is similar in both unsubstituted and core-substituted PBIs.

Compound **1** possesses an intramolecular C–H···N hydrogen bond (2.887(3) Å of C(11)···N(3) distance and 123° of C(11)–H(11A)–N(3), Table 3), which generates an S(6) ring motif (red dashed line in Fig. 3). In good agreement with this observation, the ^{1}H NMR spectrum (in $CDCl_3$) revealed a significantly downfield signal at δ 9.32 ppm (H11A, see 2.2a), giving a clear indication of the six-membered ring intramolecular hydrogen bond formation. The molecule is further stabilized by four different intramolecular C–H···O hydrogen bonds (blue dashed lines in Fig. 3 and Table 3).

Figure 4 shows the molecular packing of **1**. The crystal structure is stabilized by intermolecular π–π stacking (green dashed lines in Fig. 4) between the perylene ring and its

Table 3. Hydrogen-bond geometry (Å, °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
C(11)–H(11A)···N(3)	0.95	2.26	2.887 (3)	123
C(25)–H(25A)···O(1)	1.00	2.22	2.725 (3)	110
C(26)–H(26B)···O(2)	0.992	372	966 (4)	118
C(30)–H(30A)···O(2)	0.99	2.51	3.071 (5)	116
C(32)–H(32B)···O(3)	0.99	2.40	3.051 (9)	122
C(37)–H(37B)···O(2)[a]	0.99	2.48	3.312 (4)	141

[a] Symmetry code: $-x + 2, -y + 1, -z + 1$.

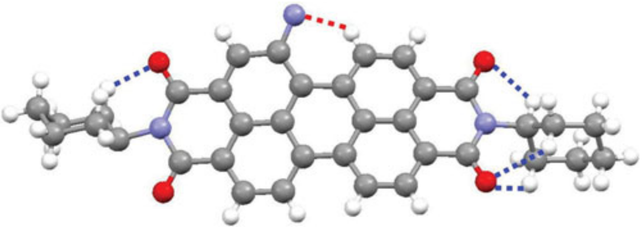


Figure 3. Crystal structure of **1**. Red and blue dashed lines denote intramolecular C–H···N and C–H···O hydrogen bonds, respectively. Two hexyl groups are omitted for clarity.

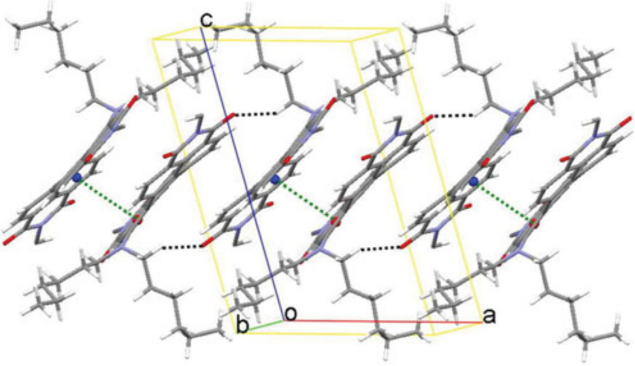


Figure 4. A packing view of **1**, viewed along the *b*-axis. Green dashed lines denote intermolecular π–π (*Cg*1–*Cg*2) interactions. *Cg*1 (red circle) and *Cg*2 (blue circle) are the centroids of the C13/C14/C19–C22 and C2/C3/C19–C12 rings, respectively. Black dashed lines denote intermolecular C–H···O hydrogen bonds. For clarity, only the PBI scaffold and the alkyl amino groups are shown.

adjacent one. The closest centroid–centroid (*Cg*1–*Cg*2) distance [symmetry code: $-x+1$, $-y+1$, $-z+1$] is 3.9635(16) Å (*Cg*1 and *Cg*2 are the centroids of the C13/C14/C19–C22 and C2/C3/C19–C12 rings, respectively). The crystal packing is further stabilized by intermolecular C–H···O hydrogen bonds (black dashed lines in Fig. 4). The C–H···O interaction links a pair of molecules into a cyclic centrosymmetric dimer that is connected to one another *via* the intermolecular π–π stacking, so linking the molecules into a continuous one-dimensional framework along the [100] direction.

Conclusions

An asymmetric dialkylamino-substituted perylene bisimide (**1**) was synthesized and characterized by single-crystal X-ray diffraction. Compound **1** crystallizes in the triclinic space group *P*–1 and possesses an intramolecular C–H···N hydrogen bond with an S(6) graph-set motif. The core twist angles of **1** are much smaller than those of disubstituted and tetrasubstituted PBIs. This twist configuration induces the axial chirality in this family of PBI dyes; the two enantiomers are observed only in the crystalline state due to the low barrier of rotation in solution. In the crystal structure, the intermolecular C–H⋯O hydrogen bond links a pair of molecules into a cyclic centrosymmetric dimer that is connected to one another *via* the intermolecular π–π stacking, so linking the molecules into a continuous one-dimensional framework along the *a*-axis. The single-crystal X-ray structure determinations described here have brought to light many interesting properties of **1**, including $\pi \cdots \pi$ stacking and intra- and inter-molecular hydrogen bonding interactions. This offers the potential for synthesizing PBI derivatives with extended molecular architectures and optical properties.

Supplementary Data

Crystallographic data for compound **1** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 1030664. Copies of these information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

The project was supported by the Ministry of Science and Technology (MOST 103-2113-M-035-001) in Taiwan. The authors appreciate the Precision Instrument Support Center of Feng Chia University for providing the fabrication and measurement facilities.

References

[1] Jones, B. A., Ahrens, M. J., Yoon, M. H., Facchetti, A., Marks, T. J., & Wasielewski, M. R. (2004). *Angew. Chem. Int. Ed.*, *43*, 6363.
[2] Würthner, F., & Stolte, M. (2011). *Chem. Commun.*, *47*, 5109.
[3] Damaceanu, M. D., Constantin, C. P., Bruma, N., & Pinteala, M. (2013). *Dyes Pigm.*, *99*, 228.
[4] Lucenti, E., Botta, C., Cariati, E., Righetto, S., Scarpellini, M., *et al.* (2013). *Dyes Pigm.*, *96*, 748.
[5] Shibano, Y., Umeyama, T., Matano, Y., & Imahori, H. (2007). *Org. Lett.*, *9*, 1971.
[6] Kozma, E., Kotowski, D., Catellani, M., Luzzati, S., Famulari, A, & Bertini, F. (2013). *Dyes Pigm.*, *99*, 329.
[7] Li, X., Sinks, L. E., Rybtchinski, B., & Wasielewski, M. R. (2004). *J. Am. Chem. Soc.*, *126*, 10810.
[8] Rybtchinski, B., Sinks, L. E., & Wasielewski, M. R. (2004). *J. Am. Chem. Soc.*, *126*, 12268.
[9] Berberich, M., Krause, A. M., Orlandi, M., Scandola, F., & Würthner, F. (2008). *Angew. Chem. Int. Ed.*, *47*, 6616.
[10] Tan, W., Li, X., Zhang, J., & Tian, H. (2011). *Dyes Pigm.*, *89*, 260.
[11] Choi, J., Lee, W., Sakong, C., Yuk, S. B., Park, J. S., & Kim, J. P. (2012). *Dyes Pigm.*, *94*, 34.
[12] Sakong, C., Kim, Y. D., Choi, J. H., Yoon, C., & Kim, J. P. (2011). *Dyes Pigm.*, *88*, 166.
[13] Daimon, T., & Nihei, E. (2013). *Materials*, *6*, 1704.
[14] Luo, M. H., & Chen, K. Y. (2013). *Dyes Pigm.*, *99*, 456.
[15] El-Daly, S. A., Alamry, K. A., Asiri, A. M., & Hussein, M. A. (2012). *J. Lumin.*, *132*, 2747.
[16] Chen, K. Y., & Chow, T. J. (2010). *Tetrahedron Lett.*, *51*, 5959.
[17] Dhokale, B., Gautam, P., & Misra, R. (2012). *Tetrahedron Lett.*, *53*, 2352.
[18] Tsai, H. Y., Chang, C. W., & Chen, K. Y. (2014). *Molecules*, *19*, 327.
[19] Ahrens, M. J., Tauber, M. J., & Wasielewski, M. R. (2006). *J. Org. Chem.*, *71*, 2107.
[20] Chen, K. Y., Fang, T. C., & Chang, M. J. (2011). *Dyes Pigm.*, *92*, 517.
[21] Chen, Z. J., Wang, L. M., Zou, G., Zhang, L., Zhang, G. J., et al. (2012). *Dyes Pigm.*, *94*, 410.
[22] Tsai, H. Y., & Chen, K. Y. (2013). *Dyes Pigm.*, *96*, 319.
[23] Zhang, X., Pang, S., Zhang, Z., Ding, X., Zhang, S., et al. (2012). *Tetrahedron Lett.*, *53*, 1094.

[24] Kong, X., Gao, J., Ma, T., Wang, M., Zhang, A., Shi, Z., & Wei, Y. (2012). *Dyes Pigm.*, *95*, 450.
[25] Tsai, H. Y., & Chen, K. Y. (2014). *J. Lumin.*, *149*, 103.
[26] Chang, C. W., Tsai, H. Y., & Chen, K. Y. (2014). *Materials*, *7*, 5488.
[27] Sheldrick, G. M. (1997). *SHELXS97, A Program for Automatic Solution of Crystal Structure*, University of Göttingen: Germany.
[28] Sheldrick, G. M. (1997). *SHELX97, A Program for Crystal Structure Refinement*, University of Göttingen: Germany.
[29] Rajasingh, P., Cohen, R., Shirman, E., Shimon, L. J. W., & Rybtchinski, B. (2007). *J. Org. Chem.*, *72*, 5973.
[30] Li, Y., Tan, L., Wang, Z., Qian, H., Shi, Y., & Hu, W. (2008). *Org. Lett.*, *10*, 529.