PERKIN 1 COMMUNICATION

Synthesis and light absorption/emission properties of novel bis-squaraine dyes with extensively conjugated π-electron systems

Shigeyuki Yagi,* Shin Murayama, Yutaka Hyodo, Yoshihiko Fujie, Msahiko Hirose and Hiroyuki Nakazumi *

Department of Applied Materials Science, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

Received (in Cambridge, UK) 18th April 2002, Accepted 14th May 2002
First published as an Advance Article on the web 27th May 2002

Novel symmetrical bis-squaraine dyes have been synthesised, in which two squaryl moieties are conjugatively linked by a phenylene or biphenyl unit. Such linkages produce significant perturbation of the absorption and fluorescence spectra in comparison with analogous symmetrical mono-squaraine dyes.

Introduction

1,3-Squaraines† (SQs), often called squaryliums, exhibit unique optical properties such as large light absorption, intense fluorescence emission, and photoconductivity, and they have been applied in the optoelectronics fields such as optical recording,[1] solar energy conversion,[2] electrophotography,[3] and emitting layers and emitting dopants in EL devices.[4] Although the limitation in synthetic methodology affording symmetrical SQ dyes[5] has suppressed the development of SQ dyes in material fields, recent achievements in preparation of unsymmetrical SQ dyes[6] and new classes of SQ homologues[7] should lead to wider utility of SQ dyes and their related compounds. Therefore, the investigation of new electronic structures of SQ derivatives should prompt research into optical and electrochemical properties for material uses. In the present paper, we report the synthesis of a series of novel bis-squaraine dyes in which two squaryl units are bridged by a phenylene or biphenyl spacer. Tuning the light absorption and fluorescence emission properties of the dyes is allowed by varying the spacer as well as the heterocyclic components at both ends of the dye skeleton.

Results and discussion

As shown in Scheme 1, the synthesis of bis-squaraine dyes **1**–**4** started from the corresponding bissquaric acids **7a**–**c**. In a similar manner to the Liebeskind's method,[8] the Pd-catalyzed cross-coupling reaction of (tributylstannyl)cyclobutenedione **5** and aromatic diiodides afforded bissquarates **6a**–**c** in 53–82% yields, which were converted to bissquaric acids **7a**–**c** by acid-promoted hydrolysis in 53–79% yields. Condensation of **7a**–**c** with heterocyclic methyl quaternary salts was carried out in butan-1-ol–benzene (4 : 1, v/v) in the presence of a small amount of quinoline or triethylamine, affording the bis-squaraine dyes **1**–**4** in 8–90% yields. The characterization by ^1H NMR, MALDI-TOF mass and IR spectra as well as elemental analysis afforded satisfactory data for each bis-squaraine dye. As shown in Fig. 1, the structure of one of the bis-squaraine dyes **1a** was confirmed by X-ray crystallographic analysis.[9] A single crystal suitable for X-ray analysis was obtained by solvent diffusion from a $CHCl_3$–MeOH solution of **1a** to diethyl ether. The structure clearly shows that two indolinylidenemethylcyclobutene moieties are introduced to the central *p*-phenylene group, and the molecule of **1a** adopts a highly planar structure: the mean deviation of the atoms in the π-conjugation (C1–C16, N1, O1, and O2) from the least-squares plane is 0.0494 Å. Therefore, **1a** possesses an extensively

Table 1 Selected bond lengths in the solid state structure of **1a** with their estimated standard deviations in parentheses

Bond	Length/Å	Bond	Length/Å
O1–C11	1.230(5)	C10–C13	1.485(6)
O2–C13	1.236(5)	C11–C12	1.444(6)
C10–C11	1.520(6)	C12–C13	1.445(6)

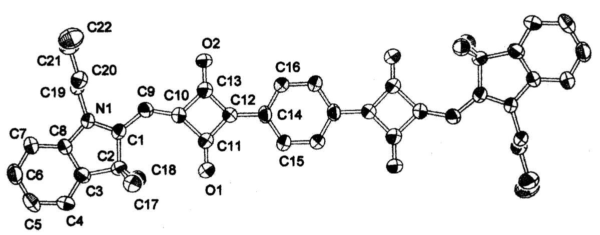
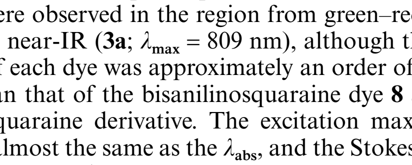


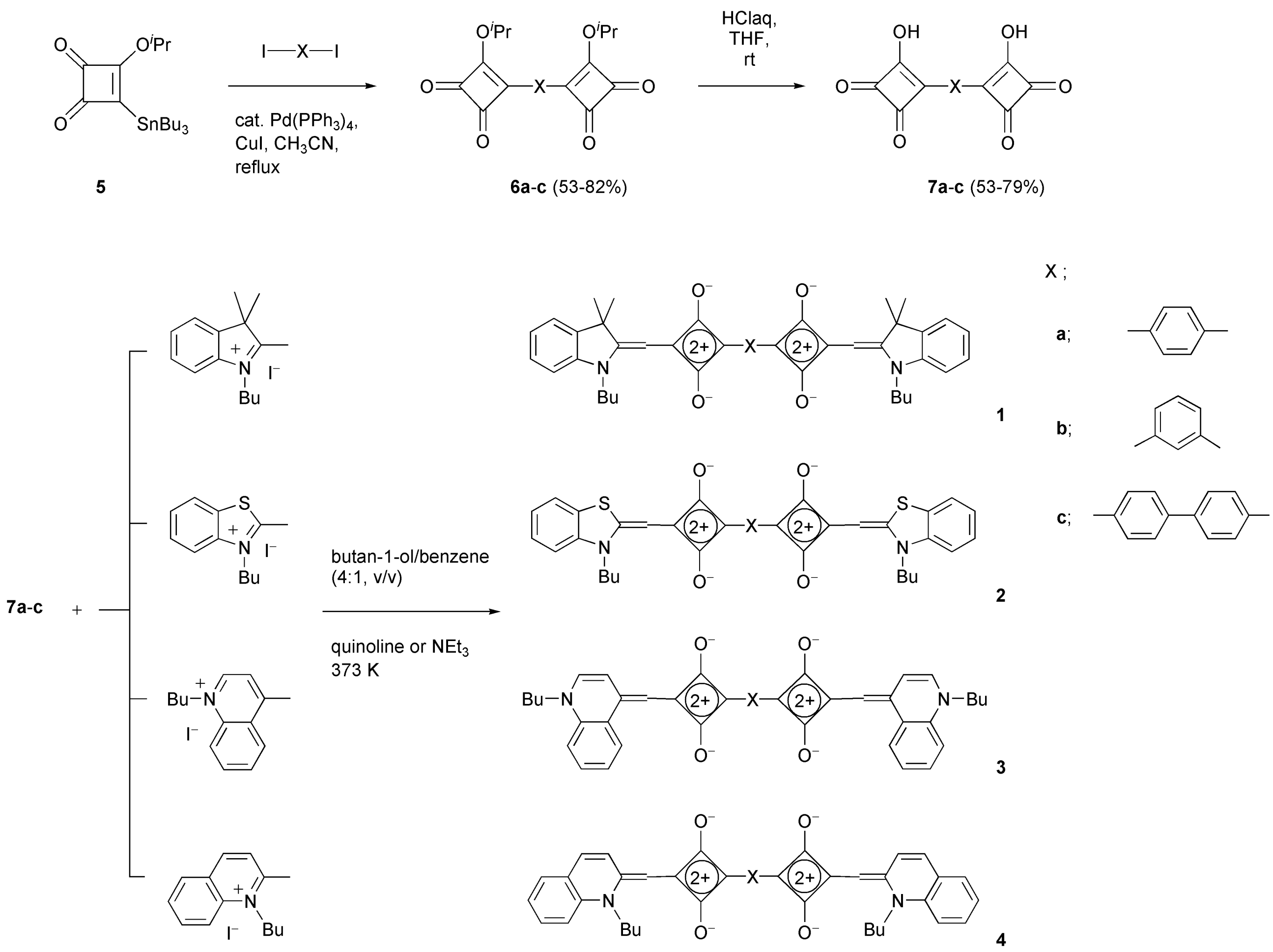
Fig. 1 The structure of the bis-squaraine dye **1a** with the atom numbering labels. Hydrogen atoms are omitted for clarity.

conjugated π-electron system. The bond lengths of O1–C11, O2–C13, C10–C13, C11–C12, and C12–C13 exhibit conjugated C=O and C=C bond characters, respectively (Table 1), whereas the C10–C11 bond is approximately a single bond. Thus, such a difference in the bond order indicates that the π-electrons in the cyclobutene rings are significantly localized.

In Fig. 2 are shown typical examples of the electronic absorption (Fig. 2a) and fluorescence emission (Fig. 2b) spectra of the bis-squaraine dyes. Various combinations of the spacer with heterocyclic moieties afforded a wide range of variation in the electronic absorption and fluorescence emission properties of the bis-squaraine dyes, as summarized in Table 2. The absorption maxima of the dyes presented here vary from green (**2b**; λ_{abs} = 543 nm in $CHCl_3$) to near-IR region (**3a**; λ_{abs} = 768 nm). The dyes bearing *p*-phenylene spacers **1a**–**4a** exhibited bathochromic shifts of λ_{abs}, compared with the dyes **1b**–**3b** and **1c**–**2c** which have *m*-phenylene and biphenyl spacers, respectively. As expected from the absorption spectra, the fluorescence emission maxima were observed in the region from green–red (**3b**; λ_{em} = 571 nm) to near-IR (**3a**; λ_{max} = 809 nm), although the emission intensity of each dye was approximately an order of magnitude smaller than that of the bisanilinosquaraine dye **8** as a typical emissive squaraine derivative. The excitation maxima of the dyes were almost the same as the λ_{abs}, and the Stokes shifts were moderate or not so large.



8



Scheme 1

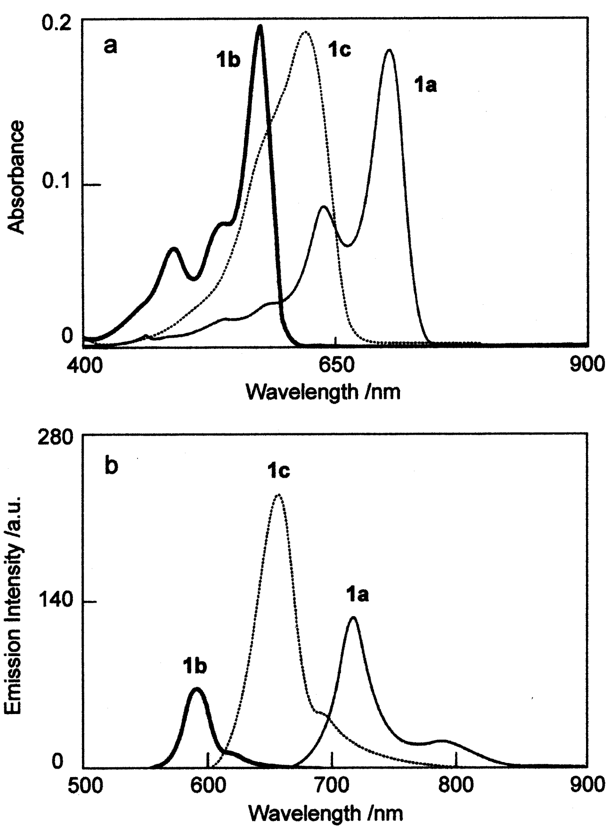


Fig. 2 (a) Electronic absorption and (b) fluorescence emission spectra of **1a**, **1b**, and **1c** in $CHCl_3$ at 25 °C. Each emission spectrum was monitored by excitation at λ_{max}.

Conclusions

In summary, the synthesis of novel bis-squaraine dyes has been demonstrated by employing bissquaric acid intermediates **7a–c** and heterocyclic methyl quaternary salts as starting materials, and their light absorption and fluorescence emission properties have been described. Various combinations of the heterocyclic components with the central aromatic ring led to tuning of absorption and fluorescence emission maxima of the dyes. Applications of the absorption and emission properties of these dyes are under investigation.

Experimental

Typical procedure for synthesis of the bis-squaraine dyes (synthesis of 1a)

To a mixture of **7a** (50 mg, 0.19 mmol) and 1-butyl-2,3,3-trimethylindolium iodide (127 mg, 0.37 mmol) in 10 mL of butan-1-ol–benzene (4 : 1, v/v) was added 0.1 mL of quinoline, and then, the mixture was heated at 100 °C for 5 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (chloroform–methanol, 10 : 1, v/v, as eluent). Further purification by recrystallization chloroform–methanol–diethyl ether afforded a crystal of **1a** (92 mg, 0.14 mmol).

1a: Yield 75%. Mp 280–281 °C (dec). IR 1567, 1606, 1731 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$–CD_3OD, 4 : 1, v/v, 25 °C) δ (ppm) = 1.04 (t, J = 7.6 Hz, 6H), 1.26–1.64 (m, 8H), 1.86 (s, 12H), 4.39 (t, J = 7.6 Hz, 4H), 6.53 (s, 2H), 7.36–8.26 (m, 8H), 8.28 (s, 4H). TOF-MS (m/z) 664 (M^+). Anal. Calcd for $C_{44}H_{44}N_2O_4$: C, 79.49; H, 6.67; N, 4.21%. Found: C, 79.29; H, 6.90; N, 3.95%.

1b: Yield, 22%. Mp 212–213 °C (dec). IR 1554, 1616, 1738 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ (ppm) = 1.02

Table 2 Electronic absorption maxima (λ_{abs}), fluorescence emission maxima (λ_{em}), and Stokes shifts ($\Delta\lambda$) of bis-squaraine dyes **1**, **2**, **3**, and **4**[a]

Dye	λ_{abs}/nm (log ε/mol^{-1} cm^{-1} dm^3)	λ_{em}/nm (relative intensity)	$\Delta\lambda^b$/nm
1a	699 (5.25), 635 (4.93)	714 (126)	22
1b	572 (5.27), 535 (4.87)	587 (56)	13
1c	618 (5.28)	656 (226)	37
2a	685 (5.28), 623 (4.99)	706 (206)	21
2b	543 (5.15), 479 (4.71)	586 (34)	15
2c	609 (5.01)	651 (157)	32
3a	768 (5.13), 692 (4.80)	809 (15)	45
3b	570 (5.30)	571 (3.4)	1
4a	704 (5.29), 641 (4.98)	736 (77)	24
8	640 (5.50)	667 (2000)	12

[a] In $CHCl_3$ at 25 °C. [dye] = 1.0×10^{-6} M. [b] $\Delta\lambda = \lambda_{em} - \lambda_{ex}$, where λ_{ex} is the wavelength of the maximum peak in the excitation spectrum.

(t, J = 7.3 Hz, 6H), 1.44–1.55 (m, 4H), 1.87 (m, 16H), 4.36 (t, J = 7.3 Hz, 4H), 6.44 (s, 2H), 7.28–7.52 (m, 9H), 8.29 (m, 2H), 9.00 (s, 1H). TOF-MS (*m*/*z*) 664 (M^+). Anal. Calcd for $C_{44}H_{44}N_2O_4 \cdot H_2O$: C, 77.39; H, 6.79; N, 4.10%. Found: C, 77.19; H, 6.85; N, 3.94%.

1c: Yield, 45%. Mp 260–261 °C (dec). IR 1556, 1616, 1739 cm^{-1}. ^1H NMR (270 MHz, $CDCl_2CDCl_2$–CD_3OD, 1 : 1, v/v, 25 °C) δ (ppm) = 1.02 (t, J = 7.6 Hz, 6H), 1.47–1.55 (m, 4H), 1.84–1.94 (m, 16H), 4.40 (t, J = 7.6 Hz, 4H), 6.50 (s, 2H), 7.51–7.58 (m, 8H), 7.79 (d, J = 8.2 Hz, 4H), 8.24 (d, J = 8.2 Hz, 4H). TOF-MS (*m*/*z*) 740 (M^+). Anal. Calcd for $C_{50}H_{48}N_2O_4$: C, 81.05; H, 6.53; N, 3.78%. Found: C, 80.85; H, 6.22; N, 3.59%.

2a: Yield, 90%. Mp 284–285 °C (dec). IR 1567, 1606, 1731 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$–CD_3OD, 4 : 1, v/v, 25 °C) δ (ppm) = 1.05 (t, J = 7.6 Hz, 6H), 1.51–1.60 (m, 4H), 1.91–2.01 (m, 4H), 4.55 (t, J = 7.6 Hz, 4H), 6.68 (s, 2H), 7.38–8.08 (m, 8H), 8.15 (s, 4H). TOF-MS (*m*/*z*) 644 (M^+). Anal. Calcd for $C_{38}H_{32}N_2O_4S_2 \cdot 1.5H_2O$: C, 67.94; H, 5.25; N, 4.17%. Found: C, 67.97; H, 5.32; N, 3.82%.

2b: Yield, 30%. Mp 279–280 °C (dec). IR 1560, 1592, 1733 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$–CD_3OD, 5 : 1, v/v, 25 °C) δ (ppm) = 1.05 (t, J = 7.6 Hz, 6H), 1.51–1.63 (m, 4H), 1.91–2.04 (m, 4H), 4.55 (t, J = 7.6 Hz, 4H), 6.69 (s, 2H), 7.42–8.22 (m, 9H), 8.23 (d, J = 8.2 Hz, 2H), 8.72 (s, 1H). TOF-MS (*m*/*z*) 644 (M^+). Anal. Calcd for $C_{38}H_{32}N_2O_4S_2 \cdot H_2O$: C, 68.86; H, 5.17; N, 4.23%. Found: C, 68.56; H, 5.54; N, 3.96%.

2c: Yield, 60%. Mp > 300 °C (dec). IR 1572, 1606, 1732 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ (ppm) = 1.05 (t, J = 7.3 Hz, 6H), 1.59–1.70 (m, 4H), 1.89–1.97 (m, 4H), 4.43 (t, J = 7.3 Hz, 4H), 6.49 (s, 2H), 7.50–7.64 (m, 4H), 7.68–7.74 (m, 6H), 7.85 (d, J = 7.3 Hz, 2H), 8.29 (d, J = 7.9 Hz, 4H). TOF-MS (*m*/*z*) 720 (M^+). Anal. Calcd for $C_{44}H_{36}N_2O_4S_2$: C, 73.31; H, 5.03; N, 3.89%. Found: C, 73.07; H, 4.87; N, 3.76%.

3a: Yield, 8%. Mp 286–287 °C (dec). IR 1575, 1614, 1716 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$–CD_3OD, 2 : 1, v/v, 50 °C) δ (ppm) = 1.04 (t, J = 7.6 Hz, 6H), 1.44–1.58 (m, 4H), 2.00–2.08 (m, 4H), 4.72 (t, J = 7.6 Hz, 4H), 7.08 (s, 2H), 7.86 (t, J = 7.3 Hz, 2H), 8.01–8.09 (m, 8H), 8.61 (d, J = 7.3 Hz, 2H), 8.66 (d, J = 8.9 Hz, 2H), 9.36 (d, J = 8.9 Hz, 2H). TOF-MS (*m*/*z*) 632 (M^+). Anal. Calcd for $C_{42}H_{36}N_2O_4 \cdot H_2O$: C, 77.52; H, 5.88; N, 4.30%. Found: C, 77.30; H, 6.14; N, 4.07%.

3b: Yield, 12%. Mp > 300 °C (dec). IR 1554, 1579, 1695 cm^{-1}. ^1H NMR (270 MHz, DMSO-d_6, 25 °C) δ (ppm) = 0.94 (t, J = 7.3 Hz, 6H), 1.37 (sext, J = 7.3 Hz, 4H), 1.79 (quint, J = 7.3 Hz, 4H), 4.42 (t, J = 7.3 Hz, 4H), 6.86 (s, 2H), 7.46 (t, J = 7.3 Hz, 2H), 7.76–7.80 (m, 3H), 7.90 (d, J = 8.6 Hz, 2H), 8.24–8.32 (m, 6H), 8.61 (d, J = 8.6 Hz, 2H), 8.93 (s, 1H). TOF-MS (*m*/*z*) 632 (M^+). Anal. Calcd for $C_{42}H_{36}N_2O_4 \cdot H_2O$: C, 77.52; H, 5.89; N, 4.30%. Found: C, 77.40; H, 5.74; N, 4.18%.

4a: Yield, 8%. Mp 227–228 °C (dec). IR 1562, 1602, 1726 cm^{-1}. ^1H NMR ($CDCl_3$–CD_3OD, 2 : 1, v/v, 50 °C) δ (ppm) = 1.13 (t, J = 7.9 Hz, 6H), 1.66–1.74 (m, 4H), 2.01–2.11 (m, 4H), 4.79 (t, J = 7.9 Hz, 4H), 6.65 (s, 2H), 7.73 (t, J = 7.9 Hz, 2H), 7.94–8.05 (m, 6H), 8.15 (s, 4H), 8.41 (d, J = 9.2 Hz, 2H), 9.55 (d, J = 9.2 Hz, 2H). TOF-MS (*m*/*z*) 632 (M^+). Anal. Calcd for $C_{42}H_{36}N_2O_4 \cdot H_2O$: C, 77.52; H, 5.89; N, 4.30%. Found: C, 77.34; H, 5.76; N, 3.98%.

References and notes

† The IUPAC name for squaric acid is dihydroxycyclobutenedione.

1 J. Fabian, H. Nakazumi and M. Matsuoka, *Chem. Rev.*, 1992, **92**, 1197 and references cited therein.

2 (*a*) V. Y. Merritt and H. Hovel, *Appl. Phys. Lett.*, 1976, **29**, 414; (*b*) D. L. Morel, K. Ghosh, T. Feng, E. L. Stogryn, P. E. Purwin, R. F. Shaw and C. Fishman, *Appl. Phys. Lett.*, 1978, **32**, 495.

3 K.-Y. Law, *Chem. Rev.*, 1993, **93**, 449, and references cited therein.

4 T. Mori, K. Miyachi, T. Kichimi and T. Mizutani, *Jpn. J. Appl. Phys.*, 1994, **33**, 6594.

5 (*a*) A. Trebs and K. Jacob, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 694; (*b*) G. Maahs and P. Hegenberg, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 888.

6 (*a*) K.-Y. Law and F. C. Bailey, *J. Org. Chem.*, 1992, **57**, 3278; (*b*) E. Terpetschnig and J. R. Lakowicz, *Dyes Pigm.*, 1993, **21**, 227; (*c*) S. Yagi, Y. Hyodo, S. Matsumoto, N. Takahashi, H. Kono and H. Nakazumi, *J. Chem. Soc., Perkin Trans. 1*, 2000, 599.

7 (*a*) H. Nakazumi, K. Natsukawa, K. Nakai and K. Isagawa, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1001; (*b*) Y. Hyodo, H. Nakazumi, S. Yagi and K. Nakai, *J. Chem. Soc., Perkin Trans. 1*, 2001, 2823; (*c*) S. Yagi, K. Nakai, Y. Hyodo and H. Nakazumi, *Synthesis*, 2002, 413.

8 (*a*) L. S. Liebeskind and R. W. Fengl, *J. Org. Chem.*, 1990, **55**, 5359; (*b*) L. S. Liebeskind, M. S. Yu, R. H. Yu, J. Wang and K. S. Hagen, *J. Am. Chem. Soc.*, 1993, **115**, 9048.

9 Crystal data of **1a**: Formula, $C_{44}H_{44}N_2O_4$; molecular weight, 664.84; crystal system, monoclinic; space group, $P21/c$; cell constants, a = 8.277(6) Å, b = 18.29(6) Å, c = 12.121(10) Å, β = 106.71(7)°; volume, 1757(6) Å^3; Z = 2; d_{calcd} = 1.256 g cm^{-3}; reflections, 2549; R = 0.0579, R_W = 0.173. CCDC reference number(s) 184342. See http://www.rsc.org/suppdata/p1/b2/b203793a/ for crystallographic files in .cif or other electronic format.