

The first structural and spectroscopic characterisation of a ring-opened form of a 2*H*-naphtho[1,2-*b*]pyran: a novel photomerocyanine†

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Cite this: *Chem. Commun.*, 2014, 50, 7900

Received 7th May 2014,
Accepted 4th June 2014

DOI: 10.1039/c4cc03435j

www.rsc.org/chemcomm

Heating 4-methoxy-1-naphthol with a 1,1-diarylprop-2-yn-1-ol gave the 2,2-diaryl-6-methoxy-2*H*-naphtho[1,2-*b*]pyran together with the novel merocyanine, (*E*)-2-[3',3'-bis(aryl)allylidene]-4-methoxynaphthalen-1(2*H*)-one. Brief UV-irradiation of the pyran favoured the formation of the (*Z*)-merocyanine with longer irradiation and/or acidic conditions favouring the (*E*)-isomer.

Naphthopyrans (benzochromenes) and fused carbocyclic and heterocyclic derivatives have attracted significant academic interest as a consequence of their photochromism which has been widely exploited in commercial photochromic ophthalmic sun-lenses.^{1,2} The photochromic properties of 3*H*-naphtho[2,1-*b*]pyrans **1** and

2*H*-naphtho[1,2-*b*]pyrans **2** (Fig. 1) have been studied and differences in their performance characteristics contrasted.³ Multi-nuclear NMR spectroscopy has been demonstrated to be a useful tool for probing photochromism⁴ and the structure of the transient merocyanine dyes resulting from the photochemically-induced electrocyclic ring-opening of 3,3-bis(4-fluorophenyl)-3*H*-naphtho[2,1-*b*]pyran have been identified as the (*Z*)- and (*E*)-1-[3,3-di(4-fluorophenyl)-allylidene]naphthalen-2(1*H*)-ones **3** and **4**, respectively;⁵ the colourless allenyl naphthol **5** (Ar = 4-FC₆H₄-) was also identified in a subsequent study.⁶

Given the commercial interest in 2*H*-naphtho[1,2-*b*]pyran derived systems² it is somewhat remarkable that there have been, to the best of our knowledge, no examples of the characterisation of the proposed merocyanine dyes (**6** and **7**) resulting from the photochemical ring-opening of the 2*H*-naphtho[1,2-*b*]pyran system **2**. Furthermore, there does not appear to have been any reports of the differing absorption properties of the isomeric merocyanine dyes. In this communication we report our findings concerning the isolation, characterisation, structure and interconversion of photomerocyanines derived from 6-methoxy-2,2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran.

Heating a mixture of 4-methoxy-1-naphthol, propynol **8a**, PPTS and trimethyl orthoformate in 1,2-dichloroethane under reflux⁷ gave a multicomponent reaction mixture, which upon elution from silica with 20% EtOAc in hexane, gave **9** (37%), a 2,2-diaryl analogue of the Brazilian hardwood (*Paratecoma alba*) extractive lapachenole,⁸ and the more polar, intensely coloured merocyanine **10** (12%) (Scheme 1). We have previously noted the formation of permanent merocyanine dyes, 4-(3,3-diaryllallylidene)naphthalen-1(4*H*)-ones,

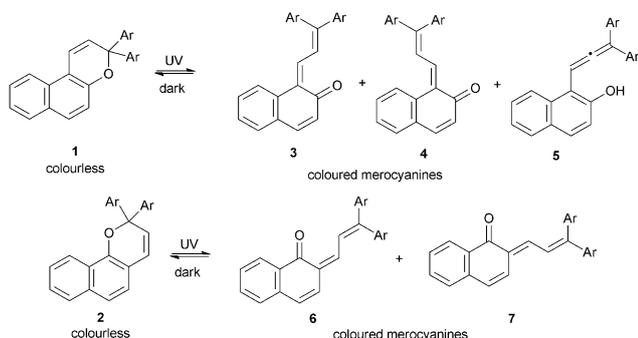


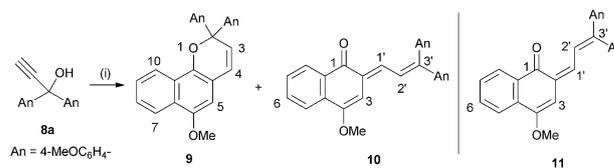
Fig. 1 Isomeric naphthopyrans and their photomerocyanine dyes.

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† Electronic supplementary information (ESI) available: Complete experimental procedures, characterization data and copies of NMR and mass spectra for all new compounds, computed Cartesian coordinates, frontier molecular orbitals and vibronic spectra. CCDC 1000252. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc03435j



Scheme 1 Naphthopyran **9** and merocyanine dyes **10** and **11**.



as by-products from the reaction between 1-naphthol and 1,1-diarylprop-2-yn-1-ols⁹ and Coelho *et al.*, have reported the formation of a related dye, 4-(3,3-diphenylallylidene)-8-hydroxynaphthalen-1(4H)-one, derived from 1,8-dihydroxynaphthalene and 1,1-diphenylprop-2-yn-1-ol.¹⁰

The ¹H NMR spectra of **9** (ESI,† Fig. S8) and **10** when recorded in CDCl₃ solution after 1 h were complex. From these spectra it was apparent that **9** underwent ring-opening to afford a mixture of **9** and **10**, together with a minor amount of an alternate merocyanine proposed as **11** (*vide infra*). Whilst the ¹H NMR spectrum of **10** in CDCl₃ solution indicated that ring-closure had occurred to afford the same equilibrium mixture of **9**, **10** and **11**. Our initial thoughts to account for this behaviour were that **9** and **10** were undergoing photochromic conversion mediated by ambient laboratory daylight resulting in an equilibrium mixture of the three species. However, when freshly preparing the ¹H NMR sample of **9** in only low levels of (ambient) laboratory lighting the same instantaneous development of the maroon colour attributed to the ring-opened species **10** (and **11**) was noted leading us to consider that it was perhaps residual acidity in the CDCl₃¹¹ which was the main contributor to the colour development. To explore this postulate a sample of commercial CDCl₃ was washed with aqueous K₂CO₃ followed by water and dried (anhyd. K₂CO₃)¹² and then used to prepare a solution of **9** under low levels of (ambient) laboratory lighting. The resulting solution was paler in colour and the ¹H NMR spectrum of **9** recorded after 1 h was quite different from the sample recorded in commercial CDCl₃ and displayed signals attributed to a ~10:1 mixture of compounds **9**:**11** (see Fig. 2 and ESI,† Fig. S10), with no evidence of **10**; a feature which implies that acidity was important for the isomerisation of **11** to **10**.

The ¹H NMR spectra of freshly prepared d₆-acetone solutions (without any protection from (ambient) laboratory daylight) of **9** and **10** were next examined (ESI,† Fig. S4 and S13). Whilst the d₆-acetone solution of **10** was deep maroon, as expected, the solution of the pyran **9** was much less intensely coloured relative to that in commercial CDCl₃ solution. The ¹H NMR spectrum of

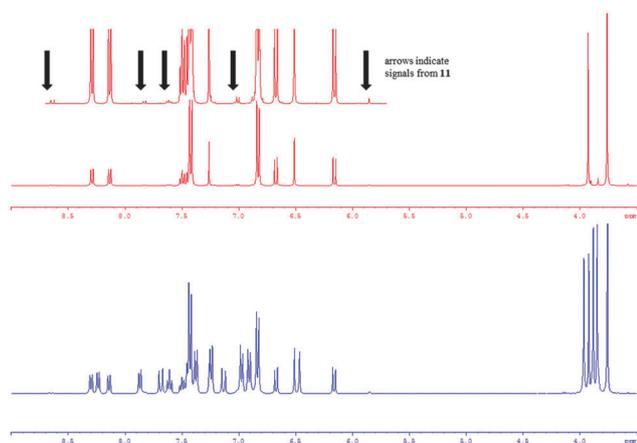


Fig. 2 ¹H NMR spectrum of **9** in commercial CDCl₃ (lower) and base washed CDCl₃ (upper) with expansion δ 5.7 \rightarrow 8.7.

9 in d₆-acetone displayed a singlet at δ 3.69 for the methoxy groups of the equivalent 4-methoxyphenyl units at C-2 and a singlet at δ 3.90 for the 6-methoxy group. The signal for 3-H appeared at δ 6.31 as a doublet ($J = 9.6$ Hz) coupled to 4-H (δ 6.77) and that for 5-H appeared as a singlet at δ 6.69. The ¹H NMR spectrum of **10** in d₆-acetone was quite different and displayed a singlet at δ 3.84, at δ 3.90 and at δ 4.02 assigned to the non-equivalent MeO groups. The protons of the allylidene side chain were unequivocally assigned by HSQC, HMBC, NOE and ¹H-¹H COSY experiments and appear at δ 7.38 (2'-H, partly obscured by other aromatic signals) and a doublet at δ 7.55 (1'-H); the magnitude of the coupling constant, $J_{1',2'} = 12.7$ Hz, consistent with an *s-trans* conformation of the allylidene unit. The ¹³C NMR spectrum displayed the expected 2-C signal at δ 82.2 for the pyran **9** in d₆-acetone and a low field signal at δ 183 confirmed the presence of the α,β -unsaturated carbonyl function in the ¹³C NMR spectrum of **10**.

To contrast with the observed isomerisation behaviour of **9** and **10** in CDCl₃ solution, treatment of a d₆-acetone solution of pyran **9** with a catalytic amount of TFA resulted in a mixture of **9**:**10**:**11** in a ratio of ~2:1:0.09, after standing over 2 h at rt (this composition remained essentially unchanged after 5 days) (ESI,† Fig. S20 and S21). Similarly treatment of a d₆-acetone solution of dye **10** with a catalytic amount of TFA resulted in the formation of essentially the same equilibrium mixture which confirms the acid-mediated isomerisation but with the implication that the dye **10** is the thermodynamically favoured ring-opened form under the applied conditions.

The structure of **10** (Fig. 3) was unequivocally determined by X-ray diffraction from a single crystal grown by slow evaporation from EtOAc/hexane solution. Bond length alternation of the (*E*)-pentadienone unit was apparent with C3–C4 (1.486 (3) Å) and C12–C13 (1.436 (3) Å) proffering single bond like character with C3–C12 (1.362 (3) Å) and C13–C14 (1.355 (3) Å) possessing more double bond character; such data is comparable with that noted for 4-(3,3-diarylylallylidene)naphthalen-1(4H)-ones.⁹ In addition to the expected propeller-like arrangement of the *geminal* 4-methoxyphenyl rings, which arise as a consequence of the minimisation of *ortho*-H-atom interactions, there is a slight deviation of the allylidene unit from the plane of the naphthalenone (torsion angle 161.09° for the allylidene unit C3–C12–C13–C14); it is possible that this deviation is a consequence of the crystal packing in which the naphthalenone rings are arranged in an anti-planar array with a naphthalenone

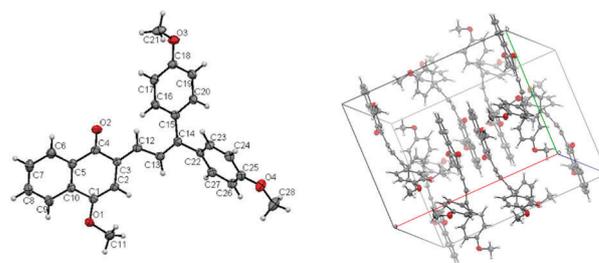


Fig. 3 Crystallographic structure of **10** (thermal ellipsoids shown at 50% probability) and crystal packing.



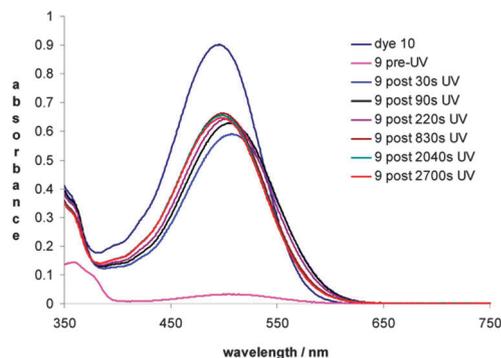


Fig. 4 Absorption spectra (acetone) of naphthopyran **9** and dye **10**.

ring centroid spacing of 3.619 Å, as the consequence of a potential dipole–dipole interaction.¹³

The photochromic response of **9** and the absorption spectrum of **10** were next examined in acetone solution. Dye **10** exhibits λ_{max} at 496 nm and has a molar extinction coefficient (ϵ_{m}) of $2.64 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ the latter is comparable to ϵ_{m} of merocyanine dyes derived from 2-tetralone¹⁴ but lower than those derived from 1-naphthol.⁹ The absorption spectrum of **9** before UV irradiation confirms the weakly coloured solution with an absorbance of <0.05 a.u. at 507 nm, whereas upon UV irradiation for 30 s a deep maroon solution was observed with an absorption maximum at 507 nm (Fig. 4). Progressively longer irradiation times resulted in a small hypsochromic shift of λ_{max} but with little if any increase in intensity after *ca.* 220 s of UV irradiation. The decay of the intensity of the absorption at 507 nm was measured as a function of time and the half-life ($t_{1/2}$) was calculated to be 42.3 min at 20 °C (Table S1, ESI†).

Of some significance was the fact that the absorption maximum of the coloured ring-opened form of pyran **9**, resulting from 30 s of UV irradiation, was bathochromically shifted by 11 nm relative to that obtained for dye **10**. It was thought that the different absorption maxima may be due to the photochemical ring-opening of the pyran **9** resulting in the alternate geometrical (*Z*)-isomer **11** of the isolated dye **10** [(*E*)-isomer] (Fig. 5).

To obtain further insight on the differences between **10** and **11**, we have used theoretical calculations (ESI† for details). For **10**, the computed geometry agrees well with XRD with deviations of *ca.* 0.01–0.02 Å. Indeed, the experimental (theoretical) C3–C4, C3–C12, C12–C13 and C13–C14 bond lengths are 1.485 (1.480), 1.362 (1.377), 1.436 (1.421) and 1.355 (1.374) Å, respectively. In **11**, these bond distances become 1.477, 1.383, 1.420 and 1.377 Å, respectively, which are similar but nevertheless show a

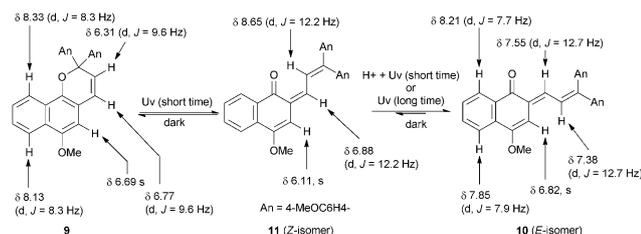


Fig. 5 Relationship between pyran **9** and dyes **10** and **11**.

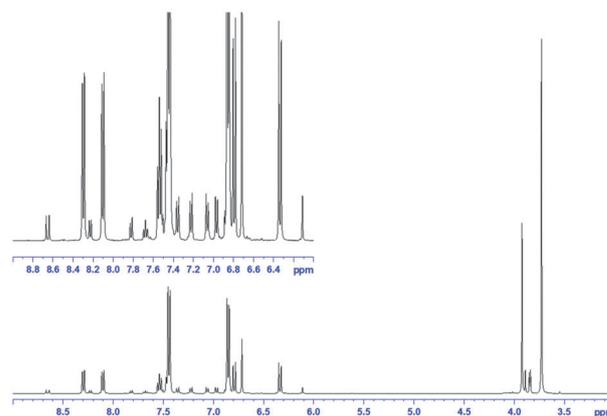


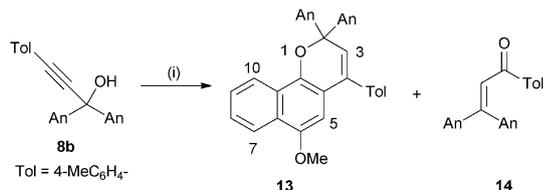
Fig. 6 ¹H NMR spectrum of naphthopyran **9** in *d*₆-acetone after 30 s UV irradiation.

slightly smaller bond length alternation, hinting at a marginally more delocalized structure. For both dyes, TD-DFT predicts a first dipole-allowed transition that can be mainly ascribed to a HOMO–LUMO contribution (see ESI† for representation). For **10**, TD-DFT predicts a first excited-state at 541 nm, with an oscillator strength, *f*, of 0.86.¹⁵ For **11**, theory predicts a small bathochromic (+11 nm or -0.05 eV, $\lambda_{\text{max}} = 552$ nm) hypochromic (-0.05 , *f* = 0.81) shift of the spectra, which seems to fit the experimental trends. To ascertain this result, we have also performed vibrationally resolved calculations of the optical spectra for each dye to reach theoretical estimates of ϵ_{m} and they also provided a weaker absorption for **11** than for **10**.

To establish the presence of proposed isomer **11**, a room temperature solution of **9** in *d*₆-acetone was subjected to UV irradiation for *ca.* 30 s. Immediately upon cessation of irradiation the ¹H NMR spectrum of the intensely coloured solution was acquired (Fig. 6). The ¹H NMR spectrum revealed new signals at δ 3.84, 3.85 and 3.89 each accounting for a methoxy group and a singlet at δ 6.11 which is attributed to 3-H. The aromatic region of the spectrum was more complex and a signal of particular note was a low field doublet resonating at δ 8.65 with a coupling constant of 12.2 Hz which has been assigned to 2'-H; the partner signal for 1'-H resonates at δ 6.88 and is obscured by other aromatic signals. Longer irradiation (40 min) of a solution of **9** in *d*₆-acetone resulted in the emergence of a further set of signals which were characteristic of the dye **10** (ESI,† Fig. S6 and S7). The ¹H NMR spectrum of a sample of dye **10** after *ca.* 40 min of UV-irradiation was also examined. Interestingly, in this instance photo-isomerization of **10** resulted in a mixture of **9**, **10** and **11** indicating that UV irradiation can affect the reverse geometrical isomerisation.

We have also used theoretical calculations to analyse the spectra of **10** and **11** (see ESI†). By looking, at the three protons of the conjugated path shown in Fig. 5, it is apparent that the measured **10**-to-**11** isomeric effects on the chemical shifts are $\Delta\delta_{(3\text{-H})} -0.71$ ($\delta 6.11$ – 6.82), $\Delta\delta_{(1'\text{-H})} -0.67$ ($\delta 6.88$ – 7.55) and $\Delta\delta_{(2'\text{-H})} +1.27$ ($\delta 8.65$ – 7.38) and theory reproduces these trends: $\Delta\delta_{(3\text{-H})} -0.62$ ($\delta 6.31$ – 6.93), $\Delta\delta_{(1'\text{-H})} -0.99$ ($\delta 7.32$ – 8.31) and $\Delta\delta_{(2'\text{-H})} +1.78$ ($\delta 9.45$ – 7.67), respectively, therefore confirming the experimental





Reagents and conditions: (i) 4-methoxy-1-naphthol, PPTS, (MeO)₂CH, 1,2-DCE, reflux

Scheme 2 Naphthopyran **12** and propenone **13**.

assignment; the differences being within the expected error bars for DFT NMR simulations.

In order to assess the influence of an aryl ring on the properties of the pyran–merocyanine dye interconversion the reaction between 4-methoxy-1-naphthol and the propynol **8b** was next undertaken. The crude reaction product resulting from this combination afforded two components after purification, the naphthopyran **12** (79%) and the propenone **13** (9%); no merocyanine dye analogous to **10** was observed (Scheme 2). The propenone **13**, formed by a Meyer–Schuster rearrangement of **8b**,¹⁶ was characterised by the presence of a signal at δ 192 for the C=O function in the ¹³C NMR spectrum and a singlet at δ 7.0 for the alkene proton in the ¹H NMR spectrum. The naphthopyran **12** displayed no discernible photochromic response at ambient temperature however; a red-purple colour was discernible when a toluene solution chilled with solid CO₂ was irradiated, but the colour faded immediately upon termination of irradiation. It is apparent that the presence of the 4-tolyl substituent favours the pyran **12**, presumably as a consequence of increased steric interactions destabilising the merocyanine species.

In summary, this report constitutes the first example of the isolation and full characterisation of a merocyanine dye derived from a 2*H*-naphtho[1,2-*b*]pyran. Furthermore, examination of the absorption spectra of the merocyanine together with a sample of irradiated naphthopyran revealed that each isomeric merocyanine has a different absorption maximum as a consequence of the different geometry; a feature which is supported by TD-DFT calculations. The presence of low concentrations of acid favours the pyran ring-opening to afford the (*E*)-photomerocyanine. The foregoing features have implications for the study of the fading kinetics and applications of photochromic compounds in commercial ophthalmic systems.

We thank the EPSRC for access to the National Mass Spectrometry Service, Swansea. A. C.-E. and D. J. acknowledge the European Research Council (ERC) and the *Région des Pays de la Loire* for financial support in the framework of a Starting

Grant (Marches-278845) and a *recrutement sur poste stratégique*, respectively. This research used resources of the GENCI-CINES/IDRIS, of the CCIPL (*Centre de Calcul Intensif des Pays de Loire*) and of a local Troy cluster.

Notes and references

- (a) U. Weigand and H. Zinner, *WO Pat.*, 2014/009020, 2014; (b) J. Takenada, J. Momoda, K. Teranishi, T. Takahashi, M. Sando and S. Izumi, *US Pat.*, 2014/0054520, 2014; (c) W. Xiao and B. Van Gemert, *WO Pat.*, 2013/090220, 2013; (d) A. Kumar, R. L. Yoest, C. Li, D. S. Jackson and H. Nguyen, *US Pat.*, 2012/0120473, 2012; (e) S. Aiken, J.-P. Cano, C. D. Gabbutt and B. M. Heron, *WO Pat.*, 2008/028930, 2008.
- (a) Y. Shimizu, S. Izumi and J. Momoda, *WO Pat.*, 2013/042800, 2013; (b) L. Sukhomlinova, T. Kosa, B. Taheri, T. White and T. Bunning, *US Pat.*, 2013/0248350, 2013; (c) D. A. Clarke, B. M. Heron, C. D. Gabbutt, J. D. Hepworth, S. M. Partington and S. N. Corns, *US Pat.*, 2002/6387512, 2002.
- (a) J. D. Hepworth and B. M. Heron, in *Functional Dyes*, ed. S.-H. Kim, Elsevier, Amsterdam, 2006, p. 85; (b) B. Van Gemert, in *Organic Photochromic and Thermochromic Compounds, Volume 1, Main Photochromic Families*, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1998, p. 111.
- S. Delbaere and G. Vermeersch, *J. Photochem. Photobiol., C*, 2008, **9**, 61.
- S. Delbaere, B. Luccioni-Houze, C. Bochu, Y. Teral, M. Campredon and G. Vermeersch, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1153.
- S. Delbaere, J.-C. Micheau and G. Vermeersch, *Org. Lett.*, 2002, **4**, 3143.
- W. Zhao and E. M. Carreira, *Org. Lett.*, 2003, **5**, 4153.
- R. Livingstone and M. C. Whiting, *J. Chem. Soc.*, 1955, 3631.
- C. D. Gabbutt, B. M. Heron, A. C. Instone, D. A. Thomas, S. M. Partington, M. B. Hursthouse and T. Gelbrich, *Eur. J. Org. Chem.*, 2003, 1220.
- L. M. Carvalho, A. M. S. Silva, C. I. Martins, P. J. Coelho and A. M. F. Oliveira-Campos, *Tetrahedron Lett.*, 2003, **44**, 1903.
- (a) J. E. Page, in *Ann. Rep. on NMR Spectroscopy*, ed. E. F. Mooney, Elsevier, Amsterdam, 1970, vol. 3, p. 149; (b) S. Florio, G. Ingrosso and R. Sgarra, *Tetrahedron*, 1985, **41**, 3091; (c) J. A. Turner and W. Herz, *J. Org. Chem.*, 1977, **42**, 1657.
- W. L. F. Armarego and C. L. L. Chai, *Purification of Laboratory Chemicals*, Butterworth-Heinemann, Elsevier, Oxford, 7th edn, 2013, p. 133.
- Single crystal X-ray diffraction data was collected on a Bruker Venture diffractometer equipped with a graphite monochromated Cu(K α) radiation source and a cold stream of N₂ gas. Selected crystal data for **10**: C₂₈H₂₄O₄, *M* = 424.47, monoclinic, *a* = 17.9087 (7) Å, *b* = 13.6467 (6) Å, *c* = 17.9157 (7) Å, β = 94.4847 (19)°, *V* = 4365.1 (3) Å³, *T* = 150 K, space group *C2/c*, *Z* = 8, μ = 0.687 mm⁻¹, 17 375 measured reflections, 4119 independent reflections (*R*_{int} = 0.0555). The final *R*₁ values were 0.0532 (*I* > 2 σ (*I*)). The final *wR*(*F*²) values were 0.1554 (*I* > 2 σ (*I*)). The final *R*₁ values were 0.0657 (all data). The final *wR*(*F*²) values were 0.1668 (all data). The goodness of fit on *F*² was 1.062. Largest peak and hole 0.267 and -0.291 e Å⁻³. See CCDC 1000252.
- C. D. Gabbutt, J. D. Hepworth, B. M. Heron, S. M. Partington and D. A. Thomas, *Dyes Pigm.*, 2001, **49**, 65.
- This reasonably fits the experimental value of 496 nm and corresponds to an error of 0.21 eV, typical of TD-DFT. See a recent review on TD-DFT benchmarks: A. D. Laurent and D. Jacquemin, *Int. J. Quantum Chem.*, 2013, **113**, 2019.
- (a) C. D. Gabbutt, B. M. Heron, C. Kilner and S. B. Kolla, *Org. Biomol. Chem.*, 2010, **8**, 4874; (b) D. A. Engel and G. B. Dudley, *Org. Biomol. Chem.*, 2009, **7**, 4149.

