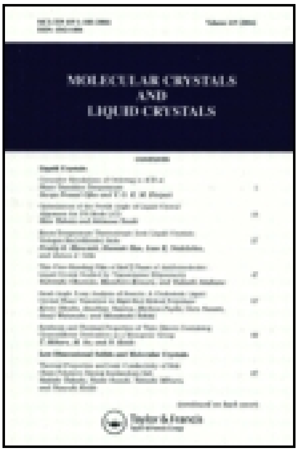

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Molecular Design and Synthesis of Novel Analogues of Benzodixanthene and Anthradichromene

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MOLECULAR DESIGN AND SYNTHESIS OF NOVEL ANALOGUES OF BENZODIXANTHENE AND ANTHRADICHROMENE

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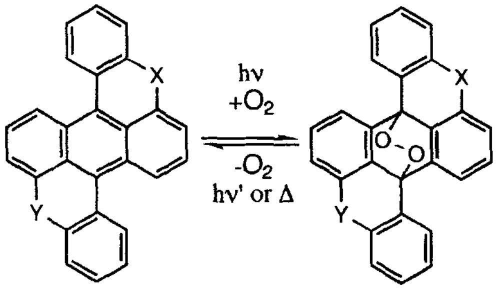
Abstract Molecular design of analogues of benzo[1,2,3-*kl*:4,5,6-*k'l'*]dixanthene and anthra[1,9-*bc*:4,10-*b'c'*]dichromene containing sulfur or nitrogen instead of oxygen was performed. The calculated absorption maxima of compounds containing oxygen or sulfur appeared in the similar region, while, those of their analogues containing nitrogen shifted to longer wavelengths. We have synthesized several new heterocyclic analogues and compared the observed wavelengths with the calculated ones.

INTRODUCTION

Benzo[1,2,3-*kl*:4,5,6-*k'l'*]dixanthene (**1a**) is famous as a thermally stable photochromic compound.[1, 2, 3] Photooxidation of the red solution of **1a** in toluene gave the colorless endoperoxide **2a**. Although compound **2a** is stable at room temperature, heating over 120 °C regenerates colored **1a** quantitatively. Anthra[1,9-*bc*:4,10-*b'c'*]dichromene (**3a**), the isomer of **1a**, is known to give similar photochromic systems between **3a** and its endoperoxide. Brauer pointed out[4] the possibility of applications of these photochromic compounds.

Derivatives or heterocyclic analogues of these compounds (**1a** or **3a**) have scarcely been reported.[2, 3] There are methyl derivatives,[5] annellated analogues,[6] and sulfur analogues[7, 8] of **1a** and sulfur analogues[9, 10] of **3a**. Among them, the absorption maximum of the annellated analogue of **1a** shifted to the longest wavelength of 574 nm,[6] however, the difference with that of **1a** (541 nm) was only 33 nm.

We have been interested in the molecular design of heterocyclic analogues of **1a** or **3a** to show sensitivity at longer wavelengths. We have predicted the absorption maxima by semi-empirical molecular orbital calculations. Heterocyclic analogues of **1d**, **1e**, **3d** and **3e** were synthesized. The observed absorption maxima of **1a**-**1e** and **3a**-**3e** were then compared with the calculated ones.



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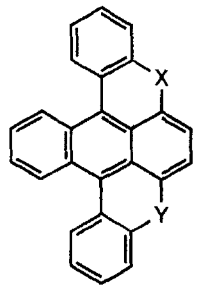


3

a X=Y=O **b** X=S, Y=O **c** X=Y=S **d** X=NPh, Y=O **e** X=Y=NPh

METHOD

Computational Method

Several studies on molecular design of photochromic compounds have been reported.[11] Nakamura and Irie have reported[12] the thermal stabilities of isomers of the diarylethene type photochromic compounds using MNDO calculations.[13] They also reported[14] the substituent effects on the absorption wavelengths based on the approximation of INDO/S.[15] Yokoyama reported[16] the prediction of absorption maxima of fulgide derivatives by PPP-PC.[17] He also reported[18] the enthalpy barrier of enantiotopomerization of fulgide by AM1 procedure.[19]

One of the authors, Tokita, predicted[3] the absorption maxima of **1a** and its analogues by PPP-PC.[17] Because these molecules are not planar in their geometries, more precise treatment has to be necessary. In this study, geometries are initially optimized by molecular mechanics[20] with CAChe.[21] After further optimization by AM1 procedure[19] absorption maxima were calculated using INDO/S.[15, 22]

Synthetic Method

Solvents and reagents were purified using literature method. Thin-layer chromatography (TLC) was performed on plastic or glass plate (10 x 5 cm) coated with Merck 5735 Kieselgel 60F. Column chromatography was performed using Wakogel C-300 (200-300 mesh, Wako Pure Chemical Industries, Ltd. 234-00085). Melting points were determined with a Büch melting point apparatus and were uncorrected. UV-VIS spectra were recorded on a Shimadzu UV-2100 spectrophotometer. IR spectra were obtained on JASCO A-302 and Perkin-Elmer 1600 FT-IR. ^{1}H-NMR spectra were recorded on Bruker AM-400 spectrometer, using tetramethylsilane as an internal standard. Elemental analyses were performed using Perkin-Elmer 240 or Yanagimoto MT-3.

RESULTS AND DISCUSSION

Calculation of Absorption Maxima

Calculated absorption maxima of **1a**, **3a** and their heterocyclic analogues (**1b**-**1e'**, **3b**-**3e'**) are shown in TABLE I. Compound **1a** and its sulfur analogues **1b** and **1c** closely resemble each other in their absorption maxima. On the other hand, the absorption maxima of nitrogen analogues **1d'** and **1e'** shifted to longer wavelengths than that of **1a**. Similarly the absorption maxima of **3d'** and **3e'** shifted to longer wavelengths than those of **3a**, **3b** and **3c**.

TABLE I First absorption maxima of **1a** or **3a** and their analogues calculated by INDO/S method.

Compd	X	Y	λ/nm	Compd	X	Y	λ/nm
1a	O	O	462	**3a**	O	O	463
1b	S	O	466	**3b**	S	O	463
1c	S	S	465	**3c**	S	S	467
1d'	NH	O	483	**3d'**	NH	O	488
1e'	NH	NH	497	**3e'**	NH	NH	514

1d'(X=NH) is a hypothetical model molecule of **1d** (X=NPh). To reduce the computational time, phenyl substituent is replaced by hydrogen. **1e'**, **3d'** and **3e'** have the same meaning.

The π-π* absorption maxima of phenol, thiophenol and aniline have been assigned[23)] as shown in TABLE II. In this case, the absorption maxima of aniline or thiophenol shifted to the direction of longer wavelengths than that of phenol. It was suggested that the introduction of more electron donating groups, -NH_2 or -SH, instead of -OH caused a bathochromic shift.

TABLE II Absorption maxima of benzene derivatives[23)]

compound	λ_{obs}/nm	solvent
phenol	211	heptane
thiophenol	236	hexane
aniline	234	hexane

TABLE III Bond lengths calculated by AM1 method

compound	bond	length/Å	standard derivation/Å
1a-1e', 3a-3e'	C-C	1.409	0.018
1a, 1b, 1d', 3a, 3b, 3d'	C-O	1.390	0.002
1b, 1c, 3b, 3c	C-S	1.687	0.003
1d', 1e', 3d', 3e'	C-N	1.397	0.004

The geometries of the sulfur analogues **1b**, **1c**, **3b** and **3c** were calculated to be fairly distorted compared with those of **1a** or **3a** because the bond lengths of C-S were longer than those of C-C, C-O, or C-N (TABLE III). This is considered to be the reason why the absorption maxima of sulfur analogues **1b**, **1c**, or, **3b**, **3c** did not shift so much to the longer wavelengths compared with those of oxygen analogues **1a**, or, **3a**, respectively.

Synthetic Routes

Symmetrical compounds **1a** and **1c** were synthesized according to the procedure of Schmidt.[1] Unsymmetrical compound **1b** was prepared as described in the reference[9]. Unsymmetrical compound **1d** was prepared according to Scheme 1.

Possible synthetic routes to compound **1e**, **1e'** and **1e''** are shown in Scheme 2.

Route I : 4→10a→11 Ullmann condensation reaction of 1,5-dichloroanthraquinone (**4**) with aniline gave **10a** in fair yield. The succeeding ring closure gave dehydrogenated product **11**. Reduction of **11** to **1e'** was not successful at this moment.

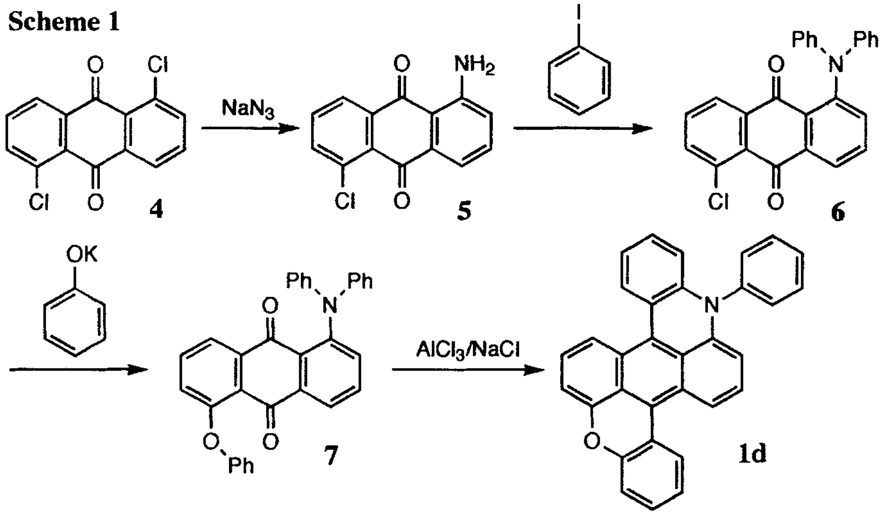
Route II : 4→10b→1e'' Ullmann condensation of **4** with *N*-methylaniline gave **10b** in good yield, however, treatment of **10a** with anhydrous aluminum chloride and sodium chloride produced an intimate mixture from which any trace of compound **1e''** could not be detected.

Route III : 8→9→1e, Route IV : 4→9→1e Too long a reaction period (over 7 days) was needed to produce **9** from 1,5-diaminoanthraquinone **8** and iodobenzene in the presence of copper bronze and potassium carbonate. Condensation reaction of 1,5-dichloroanthraquinone **4** with diphenylamine under the same condition was not practical to obtain **9** because of low reactivity.

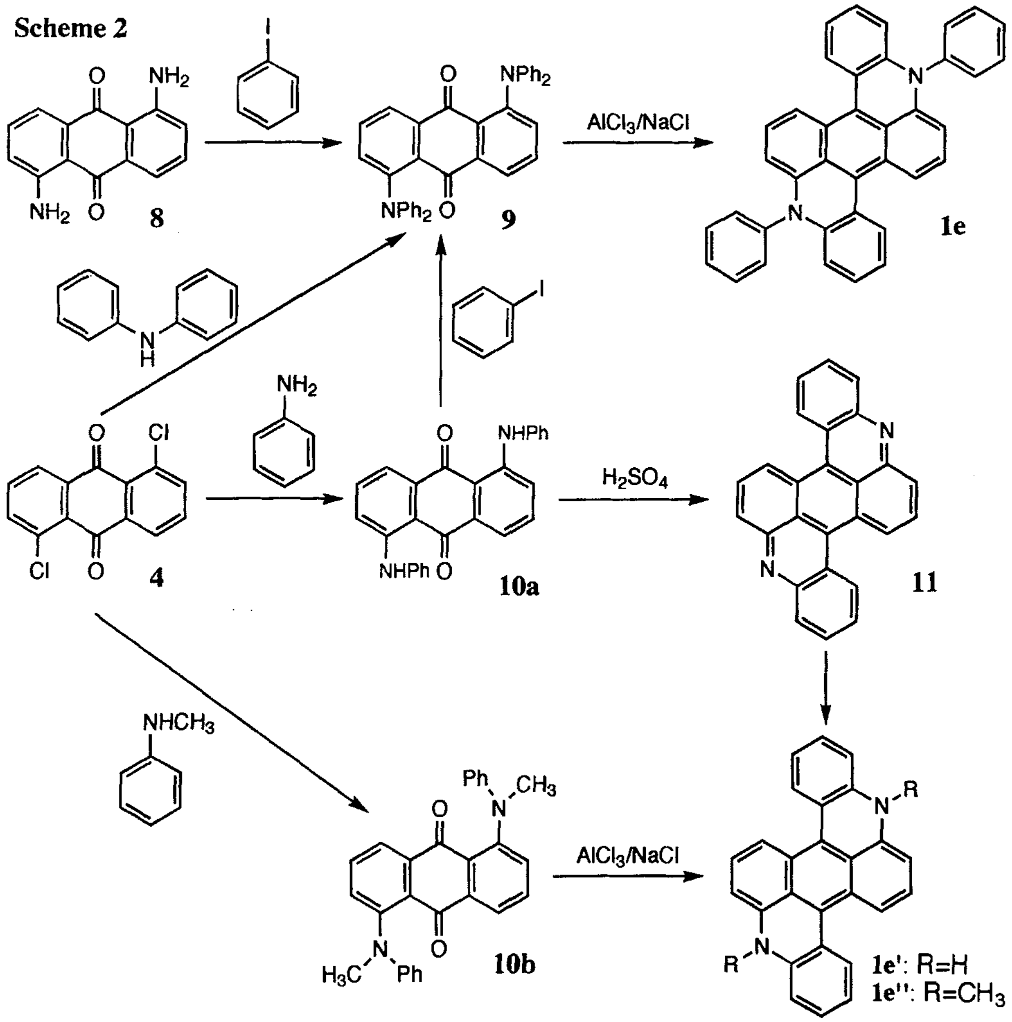
Route V : 4→10a→9→1e Ullmann condensation of **4** with 2 moles of aniline gave **10a**. Ullmann condensation of **10a** with iodobenene gave **9**, and following ring closure afforded the most practical route to compound **1e**. Total yield: 4.8%

Compound **3a**,[1] **3b**[9] and **3c**[8] were synthesized as described in the reference. Synthetic routes to compound **3d** and **3e** are shown in Scheme 3 and 4, respectively.

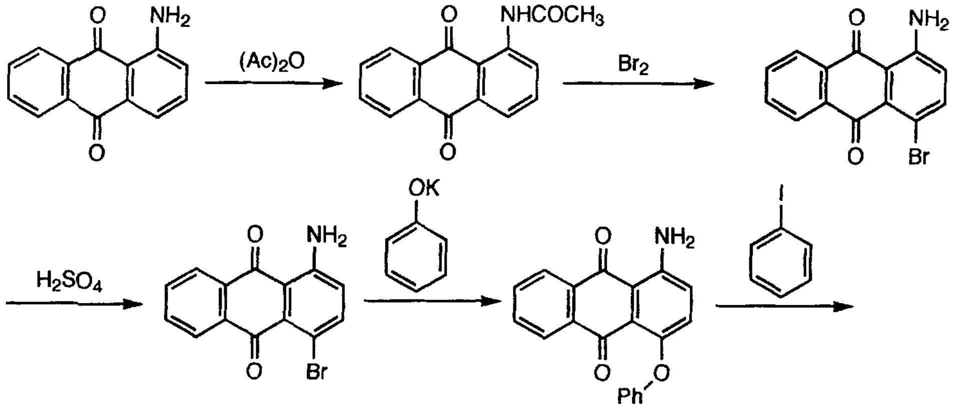
Scheme 1



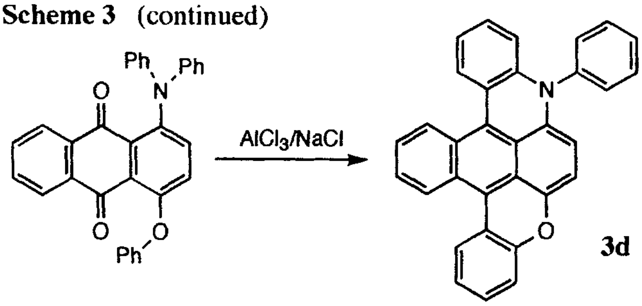
Scheme 2



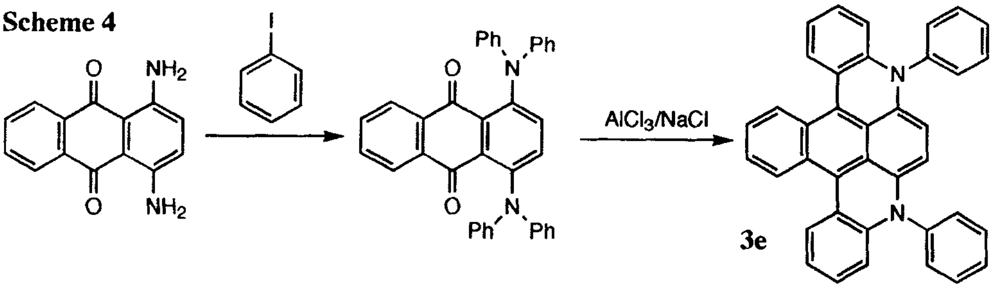
Scheme 3



Scheme 3 (continued)



Scheme 4



Correlation between Calculated Absorption Maxima and Observed Ones

Absorption spectra of **1a**, **1d** and **1e** are shown in FIGURE 1. These compounds have very similar absorption patterns. The correlation between calculated and observed wavelengths of **1a-1e** or **3a-3e** are shown in FIGURE 2. The calculated wavelengths are shorter than observed ones, however, the correlation between them may be reasonable, judging from the lines depicted in FIGURE 2. Purvis reported that calculated results by ZINDO approximation had a tendency to give similar results in many cases.$^{24)}$ There are similar reports in the series of indoaniline dyes.$^{25, 26)}$ Hiruta carefully examined the correlation in a series of polycyclic aromatic hydrocarbons and concluded that the new two-electron repulsion integral parameter (New-$\gamma^{27)}$) was especially useful for the prediction of the observed absorption maxima by Pariser-Parr-Pople approximation.$^{28)}$ We are now studying how to incorporate new parameters such as new-γ to INDO/S procedure.

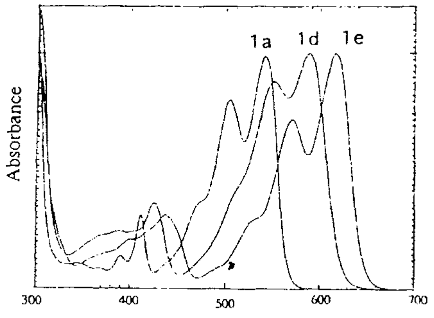


FIGURE 1 Absorption spectra of **1a**, **1d**, and **1e** in toluene.

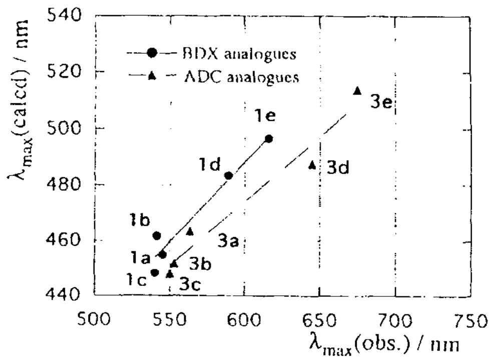


FIGURE 2 Correlation between calculated wavelengths and observed ones.

Experimental

1-(*N*,*N*'-diphenylamino)-5-chloroanthraquinone (6)

A mixture of 5[29] (1.00 g, 3.9 mmol), iodobenzene (4.00 g, 20 mmol), anhydrous potassium carbonate (1.30 g, 9.7 mmol), bromobenzene (30 ml), and copper powder (0.20 g, 3.1 mmol) was heated under reflux for 130 h. After the solvent and excess iodobenzene were removed by steam distillation, the residue was refluxed with toluene and filtered with suction to remove the inorganic part. The filtrate was purified by column chromatography (toluene/silica gel). Recrystallization from ethanol afforded **6** (981 mg, 2.39 mmol, 62%). Dark purple needles, mp 191 °C; IR(cm^{-1}/KBr) 1676 and 1251; MS (m/z) 409 (M^+), 409.87 (Mw); ^{1}H-NMR (CDCl$_3$/TMS, δ ppm) 6.94-7.04 (m, 6H), 7.19 (dd, J = 7.2, 1.4 Hz, 4H), 7.50 (dd, J = 7.9 Hz, 2H), 7.62-7.70 (m, 2H), 7.75 (dd, J = 7.7, 1.4 Hz, 1H) and 8.10 (dd, J = 7.6, 1.3 Hz, 1H).

1-(*N*,*N*'-diphenylamino)-5-phenoxyanthraquinone (7)

A mixture of **6** (600 mg, 1.46 mmol), potassium phenoxide (200 mg, 1.5 mmol), copper powder (150 mg, 2.4 mmol), and *N*,*N*-dimethylformamide (DMF) (30 ml) was heated at 170 °C for 4 h. After cooling, the mixture was poured onto 1% aqueous sodium hydroxide. The resultant precipitate was filtered with suction and dried. The residue was refluxed with toluene, filtered, and the filtrate was purified by column chromatography (toluene/silica gel). Recrystallization from toluene gave **7** (550 mg, 1.18 mmol, 81%). Red purple needles, mp 203-204 °C; IR(cm^{-1}/KBr) 3062, 1670 and 1251; MS (m/z) 467 (M^+), 467.52 (Mw); ^{1}H-NMR (DMSO-d$_6$, δ ppm) 6.94-7.02 (m, 8H), 7.15 (dd, 1H), 7.21-7.27 (m, 5H), 7.39 (dd, 2H), 7.53 (dd, 2H), 7.71 (dd, 1H), 7.83 (dd, 1H) and 7.97 (d, 1H).

16-phenyl-16-hydrobenzo[4,5,6-*kl*]xanthene[1,2,3-*k*'*l*']acridine (1d)

A mixture of **7** (100 mg, 0.21 mmol), hydroquinone (1.47 mg, 0.108 mmol), anhydrous aluminum chloride (1.5 g, 11.1 mmol), and anhydrous sodium chloride (165 mg, 2.79 mmol), was heated at 150 °C for 3 h. After cooling, 1.0 M hydrochloric acid was added carefully and filtered with suction. The residue was washed with a solution of sodium dithionite (2.00 g) and sodium hydroxide (1 g) in water (50 ml). After drying over P_2O_5, the residue was dissolved in toluene and purified by column chromatography (toluene/activated basic alumina) during hot. Repeated column chromatography (toluene/activated alumina) in the dark and further recrystallization from benzene gave **1d** (37.8 mg, 0.087 mmol, 41%). Purple needles, mp 210 °C; IR(cm^{-1}/KBr) 3051, 1305 and 1251; MS (m/z) 433 (M^+), 433.49 (Mw); ^{1}H-NMR (DMSO-d$_6$, δ ppm) 5.78 (d, $J_{d\text{-}e}$ = 7.6 Hz, 1H, d), 6.28 (dd, $J_{q\text{-}p}$ = 7.4 Hz, 1H, q), 7.00 (d, $J_{k\text{-}l}$ = 7.3 Hz, 1H, k), 7.04 (dd, $J_{o\text{-}m}$ = 7.2 Hz, $J_{o\text{-}p}$ = 7.6 Hz, 1H, o), 7.16-7.27 (m, 4H, e, h, j, p), 7.33-7.41 (m, 2H, i, l), 7.51 (dd, $J_{a\text{-}b}$ = 7.3 Hz, 2H, a), 7.67 (dd, $J_{c\text{-}b}$ = 7.3 Hz, 1H, c), 7.78-7.85 (m, 3H, b, f), 8.04 (dd, $J_{m\text{-}l}$ = 8.8 Hz, 1H, m), 8.13 (dd, $J_{n\text{-}o}$ = 7.5 Hz, 1H, n) and 8.21 (dd, $J_{g\text{-}h}$ = 8.1 Hz, 1H, g); UV-VIS (nm in toluene (log ε)) 589 (4.33), 551 (4.27) and 425 (3.87); Fluorescence (nm) 612 (ex.592).

Ring closure reaction to **1e**, **3d**, **3e** were similarly performed.

1e Yield: 40%, mp 329-330 °C; MS (m/z) 508 (M^+), 508.62(Mw); IR(cm^{-1}/KBr) 3061, 1447, 1276 and 699; ^{1}H-NMR (DMSO-d$_6$, δ ppm) 5.69 (d, J = 7.7 Hz, 2H, acridine c), 6.19 (d, J = 8.2 Hz, 2H, acridine d), 6.96 (dd, J = 7.5 Hz, J= 7.6 Hz, 2H, acridine f), 7.03 (dd, J = 7.9 Hz, J = 8.6 Hz, 2H, acridine b), 7.10 (dd, J = 8.0 Hz, 2H, acridine e), 7.49 (d, J = 8.3 Hz, 4H, phenyl h), 7.65 (dd, J = 7.1 Hz, J = 7.9 Hz, 2H, phenyl j), 7.72 (d, J = 8.6 Hz, 2H, acridine a), 7.79 (dd, J = 7.4 Hz, J = 7.8 Hz, 2H, phenyl j), 8.14 (d, J = 7.9 Hz, 2H, acridine g); UV-VIS (nm in toluene (log ε)) 616 (4.45), 569 (4.31) and 4.37 (3.96).

3d Yield: 16%; mp 221-222 °C; IR(cm^{-1}/KBr) 1440 and 750; ^{1}H-NMR (DMSO-d$_6$, δ ppm) 5.44 (d, J = 8.3 Hz, 1H), 6.09 (d, J = 8.3 Hz, 1H), 6.50 (d, J = 8.3 Hz, 1H), 6.94 (pseudo-t, 1H), 6.98 (d, J = 8.0 Hz, 1H), 7.08 (pseudo-t, 1H), 7.13 (pseudo-t, 1H), 7.24 (pseudo-t, 1H), 7.44 (d, J = 7.6 Hz, 2H), 7.45 (m, 1H), 7.50 (m, 1H), 7.61 (t = 7.6 Hz, 1H), 7.74 (pseudo-t, 2H), 7.78 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 8.36 (pseudo-t, 1H) and 8.38 (pseudo-t, 1H); MS (m/z) 433 (M^+), 430.51 (Mw); UV-VIS (nm in toluene (log ε)) 645 (4.00), 608 (4.03), 437 (3.80), 342 (4.09) and 300 (4.43).

3e Yield: 3%; mp 349-351 °C; IR(cm^{-1}/KBr) 1550, 1490, 1280 and 700; UV-VIS (nm in toluene (log ε)) 675 (3.97), 456 (3.88), 351 (4.30) and 304 (4.37).

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