

## Oxidative electrochemical aryl C–C coupling of spiropyrans†

Cite this: *Chem. Commun.*, 2013, 49, 6737Received 2nd April 2013,  
Accepted 11th June 2013

DOI: 10.1039/c3cc42396d

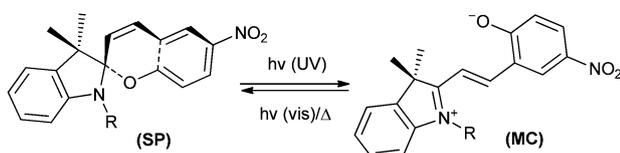
www.rsc.org/chemcomm

Oleksii Ivashenko,<sup>†a</sup> Jochem T. van Herpt,<sup>†b</sup> Petra Rudolf,<sup>a</sup> Ben L. Feringa<sup>ab</sup> and Wesley R. Browne<sup>\*ab</sup>

The isolation and definitive assignment of the species formed upon electrochemical oxidation of nitro-spiropyran (SP) is reported. The oxidative aryl C–C coupling at the indoline moiety of the SP radical cation to form covalent dimers of the ring-closed SP form is demonstrated. The coupling is blocked with a methyl substituent *para* to the indoline nitrogen.

Since its discovery in 1952 by Fischer and coworkers,<sup>1</sup> the reversible photochemistry of spiropyrans (SP) has seen widespread application,<sup>2–4</sup> building on their solvato- and acidochromism and their sensitivity to certain metal ions,<sup>5</sup> providing systems with dual, triple or even quadruple<sup>6</sup> stimuli responsiveness. The ring-closed SP form is neutral and non-planar and is converted by irradiation with UV light to its thermally unstable merocyanine (MC) zwitterionic planar form (Fig. 1).

The redox chemistry of spiropyrans has received much less attention than their photochemistry, despite several reports of electrochromism both in solution and on surfaces.<sup>7–9</sup> The oxidative electrochemistry is characterized by an irreversible oxidation at *ca.* 1.05 V (Fig. 2a) and mechanisms for the processes that follow oxidation were first proposed over a decade ago.<sup>10–12</sup> It was established that the oxidation is centred on the indoline moiety of the



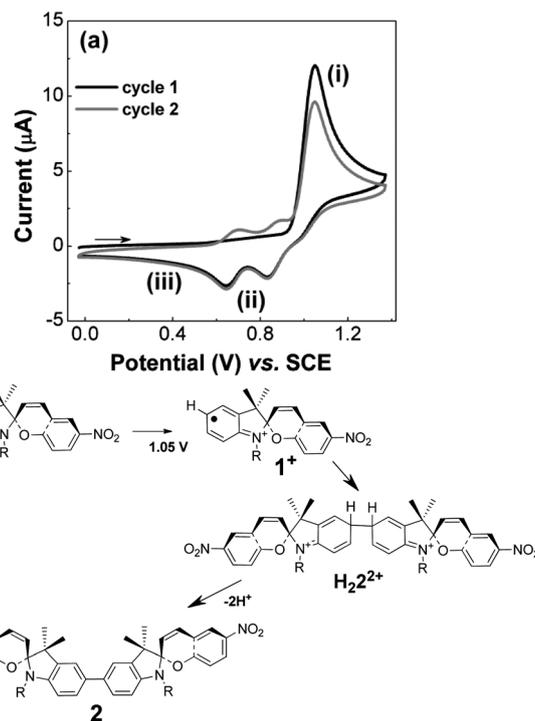
**Fig. 1** 'Ring-closed' spiropyran (SP) and 'ring-open' merocyanine (MC) forms of **1**. R is  $-\text{C}_2\text{H}_4-\text{OC}(=\text{O})-\text{C}_7\text{H}_{15}$ .

<sup>a</sup> Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. E-mail: w.r.browne@rug.nl; Tel: +31 50 363 4428

<sup>b</sup> Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

† Electronic supplementary information (ESI) available: Synthesis and spectroscopy of compounds **1–3**. See DOI: 10.1039/c3cc42396d

‡ These authors have contributed equally to this manuscript.



**Fig. 2** (a) Cyclic voltammetry of **1** at a glassy carbon (GC) electrode in 1,2-dichloroethane (0.1 M TBAPF<sub>6</sub>). (b) The oxidation at 1.05 V is overall a four-electron ECCE process, E: 1 e<sup>−</sup> oxidation of (two equiv. of) **1**, C: dimerization of **1** by aryl C–C coupling to form H<sub>2</sub>2<sup>2+</sup>, C: double deprotonation to form **2**, E: 2 e<sup>−</sup> oxidation of **2** to form 2<sup>2+</sup>. At point (ii) and (iii), 2<sup>2+</sup> undergoes 1 e<sup>−</sup> reduction to 2<sup>•+</sup> and **2**, respectively.

SP,<sup>10,12</sup> which was then proposed to undergo fast isomerization to a ring-open MC radical cation. The oxidized open form was proposed to undergo rapid irreversible coupling to form a C–O–C<sup>12</sup> or C–O–O–C link between the phenol moieties of two molecules of MC<sup>•+</sup> (Fig. S1a, b, ESI†).<sup>13</sup> Recently it has been proposed that π-radical cation dimers of the MC form are obtained upon electrochemical oxidation and that neutral π-dimers are obtained upon subsequent reduction (Fig. S2c, ESI†).<sup>14,15</sup> An important observation, with regard to dimerization, is that encapsulation of SP in a porous matrix (*i.e.*, zeolites or mesoporous silicates) renders the voltammetry of

spiropyran partially or even fully reversible.<sup>13</sup> Although this supports a dimerization model, ring-opening to the MC form upon oxidation was not observed when the SP was trapped.<sup>13</sup> Other mechanisms have been proposed also,<sup>2</sup> however, definitive assignments of the processes involved and species formed have, until now, not been made, despite the effective utilisation of SP in redox responsive systems, e.g., sensors, molecular logic, requiring a clear understanding of the processes involved.

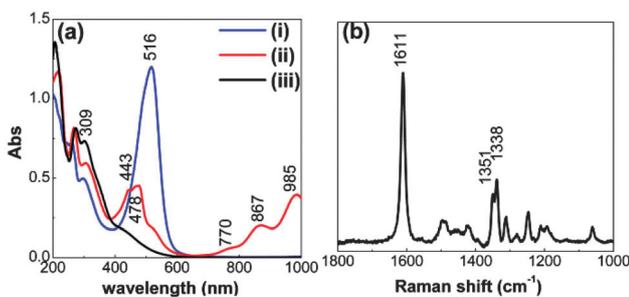
Here, we demonstrate that oxidation of nitro-BIPS spirocyan (1, Fig. 1), contrary to previous proposals (Fig. S1, ESI<sup>†</sup>), in fact results in the formation of covalent SP–SP dimers as a product of oxidative carbon–carbon bond formation at the 'para' position of the indoline moieties, to form a spirocyan dimer 2 (an ECCE<sup>16</sup> mechanism, Fig. 2b). Isolation and spectroscopic characterisation of 2, provides definitive assignment of the mechanisms associated with the voltammetry of 1 (Fig. 2a). Furthermore, we show that oxidative dimerization can be blocked by introducing a methyl substituent in the indoline unit (3) and confirm that oxidation of 1–3 does not lead to ring-opening to the MC form.

In the first positive sweep in the CV of 1, irreversible oxidation of the indoline nitrogen occurs at 1.05 V (Fig. 2a), followed by a reversible two step reduction at 0.83 V and 0.65 V on the reverse sweep. The second cycle features two oxidation waves of the product 2 and a decrease in the oxidation at 1.05 V.<sup>17</sup>

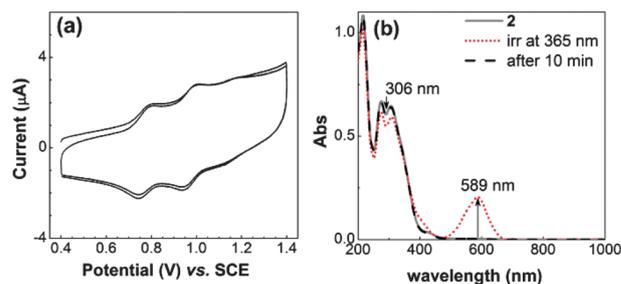
UV/vis absorption spectroelectrochemistry shows that upon oxidation of 1 (Fig. 3a(i)) an absorption band appears at 516 nm (with a shoulder at ca. 488 nm, Fig. 3a). The spectrum is consistent with the spectrum reported for the dication of *N,N,N',N'*-tetramethylbenzidine (TMB<sup>2+</sup>, *vide infra*).<sup>18</sup> Subsequent reduction at 0.83 V (Fig. 2a(ii)) results in a decrease in absorbance at 516 nm and the appearance of new absorption bands at 443 nm, 478 nm, 770 nm, 867 nm and 985 nm.<sup>19</sup>

The resonance Raman spectrum of 2<sup>•+</sup> (Fig. 3b) shows an intense band at 1611 cm<sup>-1</sup>, assigned, tentatively, to an aromatic C=C stretching mode and N-ring stretching mode of the indoline unit at 1351 cm<sup>-1</sup> by comparison with the Raman spectrum reported for TMB<sup>•+</sup>.<sup>20,21</sup> Reduction to form 2 results in a complete loss in NIR absorbance and an increase in absorption at 308 nm with a weak absorbance tailing into the visible region.

Preparative oxidative electrolysis of 1 at 1.2 V, followed by isolation and purification of the products obtained upon subsequent reduction at 0.2 V yielded 2 as the major product (Fig. 2b). Compound 2 was separated from unreacted 1 by column



**Fig. 3** (a) UV/vis absorption spectra of the product formed upon oxidation of 1 in CH<sub>3</sub>CN (0.1 M NaClO<sub>4</sub>) at (i) 1.2 V, and subsequent reduction at (ii) 0.8 V and (iii) 0.2 V. (b) Resonance Raman spectrum ( $\lambda$  785 nm) of the radical cation 2<sup>•+</sup>.



**Fig. 4** (a) CV of 2 at a GC electrode in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M TBAPF<sub>6</sub>). (b) UV/vis absorption spectra of 2 in CH<sub>3</sub>CN before (grey line) and after irradiation at 365 nm (red dotted line) and following thermal recovery of the original 2 spectrum (black dashed line).

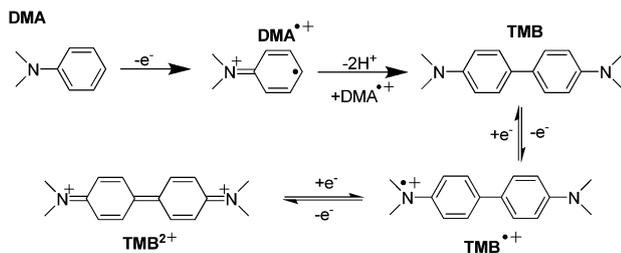
chromatography and characterised by <sup>1</sup>H NMR, ATR-FTIR, UV/vis absorption and Raman spectroscopy, ESI-MS and cyclic voltammetry (see ESI<sup>†</sup> for details). The cyclic voltammetry of 2 is shown in Fig. 4a. Two reversible oxidations are observed at 0.8 V and 1.0 V that are coincident with the redox waves those observed after the initial oxidative sweep for 1 (Fig. 2a).

The mass of 2, 955.6 *m/z*, is in agreement with loss of H<sub>2</sub> and dimer formation (*i.e.* [1<sub>2</sub>-H<sub>2</sub>]). The <sup>1</sup>H NMR spectrum of 2 is similar to that of 1 indicating that it is in the ring-closed spirocyan form (see ESI<sup>†</sup>). Importantly 2 shows one signal less in the aromatic region and a change in the coupling pattern for the indoline moiety indicating symmetric dimerization through formation of a phenyl–phenyl bond between the indoline units. These observations are in agreement with earlier reports of Cu(II) mediated dimerization (*vide infra*).<sup>5</sup>

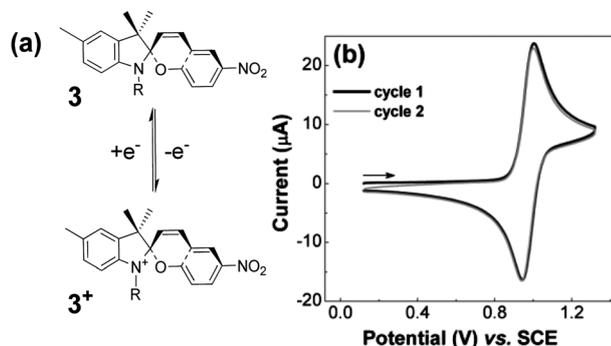
As for the <sup>1</sup>H NMR spectra, the ATR FTIR spectra of 1 and 2 (Fig. S4, ESI<sup>†</sup>) are essentially the same with only minor differences in the absorption band assigned to an aromatic C=C stretching mode, which shifts from 1608 cm<sup>-1</sup> for 1 to 1613 cm<sup>-1</sup> for 2. The band assigned to the nitro stretch at 1338 cm<sup>-1</sup> and the spiro carbon mode at 956 cm<sup>-1</sup> are unaffected by dimerization as expected.<sup>22,23</sup> Importantly the characteristic absorption of the ring-closed form<sup>24</sup> (*i.e.* the spirocyan form) at 956 cm<sup>-1</sup> indicates that 2 is formed in the ring-closed SP state, and not the ring-open MC form, consistent with <sup>1</sup>H NMR spectroscopic data (*vide supra*). The UV/vis absorption spectrum of 2 and the changes observed upon irradiation at 365 nm confirm that the spirocyan form of 2 is obtained upon oxidation of 1. Irradiation of 2 in acetonitrile at 365 nm results in the appearance of an absorption band in the visible region at 589 nm, with recovery of the original spectrum thermally (Fig. 4).

The mechanism by which 2 forms upon oxidation of 1 (Fig. 2b) can be understood by considering the electrochemistry of the structurally analogous *N,N*-dimethylaniline (DMA) – which represents the indoline unit of the spirocyan. DMA has already been shown to undergo oxidative dimerization (Scheme 1).<sup>25–27</sup>

Briefly, oxidation of DMA at 0.76 V vs. SCE<sup>16</sup> yields initially the radical cation DMA<sup>•+</sup>, which undergoes dimerization *via* aryl–aryl C–C homocoupling. This is immediately followed by loss of two protons to yield the neutral species *N,N,N',N'*-tetramethylbenzidine (TMB). TMB undergoes two one-electron oxidation steps (TMB ↔ TMB<sup>•+</sup> ↔ TMB<sup>2+</sup>). Hence an analogous mechanism can be proposed for the formation of 2 from 1 (Fig. 2b). Indeed very recently, Natali *et al.* have reported that a related nitro-BIPS compound reacts with Cu(II) salts to form radical cations,<sup>5</sup> which subsequently dimerise *via* an aryl



**Scheme 1** Mechanism for electrochemical oxidative dimerization of *N,N*-dimethylaniline (DMA) to *N,N,N',N'*-tetramethylbenzidine (TMB). The dimer obtained can be oxidized to monocationic and dicationic states.



**Fig. 5** CV of **3** in acetonitrile (0.1 M TBAPF<sub>6</sub>) at a GC electrode at a scan rate of 0.1 V s<sup>-1</sup>.  $I_{pa} = I_{pc}$  and  $E_{pa} - E_{pc} = 60$  mV.

carbon-carbon coupling, to form the symmetrical dimer of the ring-closed spiropyran (SP).

Since oxidation of nitro-spiropyran **1** produces a reactive radical cation, which undergoes rapid C-C coupling at the *para*-position of the aromatic indoline moiety, we anticipated and indeed found that when the *para* position bears a methyl group (methyl-nitro-spiropyran **3**), a stable cationic species is generated upon oxidation – the methyl groups block dimerization – and reversible electrochemistry is observed (Fig. 5).

The solid state Raman spectra of **1** and **3** are similar, as expected (Fig. S5, ESI<sup>†</sup>). For both **1** and **3**, the strongest features in the spectrum are from the symmetric and asymmetric nitro-aromatic stretching modes at 1335 cm<sup>-1</sup> and 1574 cm<sup>-1</sup>, respectively. Other bands typical of ring-closed spiropyran **1** at 1230 cm<sup>-1</sup> and 1650 cm<sup>-1</sup> are present also.

The UV/vis absorption spectrum of **3** shows a maximum absorbance at 341 nm and no absorption in the visible region, as for **1** (Fig. S6, ESI<sup>†</sup>). Oxidation at 1.2 V results in a decrease in absorbance at 341 nm and a concomitant increase in absorbance at 306 nm and *ca.* 457 nm. Subsequent reduction at 0.4 V resulted in reformation of the initial spectrum. Hence, the additional methyl group renders the oxidation of SP reversible and shows that oxidation does not lead to ring-opening to the MC form.

We have demonstrated that one-electron electrochemical oxidation of SP **1** to form an indoline centred radical cation is followed by rapid and irreversible dimerization. In contrast to previous proposals we have shown that dimerization proceeds *via* aryl C-C coupling of the indoline units to form a symmetric

dimer with a ring-closed, spiropyran structure. Importantly, we demonstrate that the species observed spectroscopically upon oxidation are the oxidised states of the already dimerized species (**2**) and not of oxidised or ring-opened merocyanine monomers. Furthermore, we have shown that the dimer formed exhibits reversible photochemical ring-opening.

In a broader context, the irreversible formation of **2** by oxidation of **1** can be considered as permanent writing of a state for which the reversible oxidation waves of **2** at less positive potential could serve as a convenient readout modality, electrochemically and spectroscopically, given the strong NIR absorption of the monocation **2**<sup>+</sup>. In addition the photochromic response of **1** is retained in **2** enabling temporary information storage regardless of whether it is in the monomer or dimer form.

The “Top Research School” (Bonus Incentive Scheme, the Netherlands’ Ministry of Education, Science, and Culture) and the ERC (Adv.G. 227897, JTH, BLF) are thanked for funding.

## Notes and references

- 1 E. Fischer and Y. Hirshberg, *J. Chem. Soc.*, 1952, 4522.
- 2 B. L. Feringa and W. R. Browne, *Molecular Switches*, John Wiley & Sons, 2011.
- 3 I. Willner, M. Lion-Dagan and E. Katz, *Chem. Commun.*, 1996, 623.
- 4 A. Koçer, M. Walko, W. Meijberg and B. L. Feringa, *Science*, 2005, **309**, 755.
- 5 M. Natali and S. Giordani, *Org. Biomol. Chem.*, 2012, **10**, 1162.
- 6 S. Guragain, B. P. Bastakoti, M. Ito, S. Yusa and K. Nakashima, *Soft Matter*, 2012, **8**, 9628.
- 7 A. Doron, E. Katz, G. Tao and I. Willner, *Langmuir*, 1997, **13**, 1783.
- 8 R. Baron, A. Onopriyenko, E. Katz, O. Lioubashevski, I. Willner, S. Wang and H. Tian, *Chem. Commun.*, 2006, 2147.
- 9 P. Mialane, G. Zhang, I. M. Mbomekalle, P. Yu, J.-D. Compain, A. Dolbecq, J. Marrot, F. Sécheresse, B. Keita and L. Nadjo, *Chem.-Eur. J.*, 2010, 5572.
- 10 M. Campredon, G. Giusti, R. Guglielmetti, A. Samat, G. Gronchi, A. Alberti and M. Benaglia, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2089.
- 11 J. F. Zhi, R. Baba and A. Fujishima, *Ber. Bunsen Ges.*, 1996, **100**, 1802.
- 12 M. J. Preigh, M. T. Stauffer, F. T. Lin and S. G. Weber, *Faraday Trans.*, 1996, **92**, 3991.
- 13 A. Doménech, H. García, I. Casades and M. Esplá, *J. Phys. Chem. B*, 2004, **108**, 20064.
- 14 K. Wagner, R. Byrne, M. Zanoni, S. Gambhir, L. Dennany, R. Breukers, M. Higgins, P. Wagner, D. Diamond, G. G. Wallace and D. L. Officer, *J. Am. Chem. Soc.*, 2011, **133**, 5453.
- 15 O. Oms, K. Hakouk, R. Dessapt, P. Deniard, S. Jobic, A. Dolbecq, T. Palacin, L. Nadjo, B. Keita, J. Marrot and P. Mialane, *Chem. Commun.*, 2012, **48**, 12103.
- 16 ‘E’ = electron transfer, ‘C’ = chemical.
- 17 The CV of **1** under inert atmosphere (O<sub>2</sub>, H<sub>2</sub>O ≤ 1 ppm) is identical to that in air, excluding involvement of water or oxygen.
- 18 H. Hasegawa, *J. Phys. Chem.*, 1961, **65**, 292.
- 19 Y. Hirata, M. Takimoto and N. Mataga, *Chem. Phys. Lett.*, 1983, **97**, 569.
- 20 V. Guichard, A. Bourkba, O. Poizat and G. Buntinx, *J. Phys. Chem.*, 1989, **93**, 4429.
- 21 L. Boilet, G. Buntinx, C. Lapouge, C. Lefumeux and O. Poizat, *Phys. Chem. Chem. Phys.*, 2003, **5**, 834.
- 22 M. De Backer and F. X. Sauvage, *J. Electroanal. Chem.*, 2007, **602**, 131.
- 23 G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, John Wiley & Sons, Ltd, Chichester, UK, 3rd edn, 2001.
- 24 R. Delgado-Macuil, M. Rojas-López, V. L. Gayou, A. Orduña-Díaz and J. Díaz-Reyes, *Mater. Charact.*, 2007, **58**, 771.
- 25 T. Mizoguchi and R. N. Adams, *J. Am. Chem. Soc.*, 1962, **84**, 2058.
- 26 Z. Galus, R. M. White, F. S. Rowland and R. N. Adams, *J. Am. Chem. Soc.*, 1962, **84**, 2065.
- 27 H. Yang, D. O. Wipf and A. J. Bard, *J. Electroanal. Chem.*, 1992, **331**, 913.