Novel photo-responsive organic spin systems: preparation and properties of norbornadienes and spiropyrans with TEMPO radical substituents

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Several photo-responsive norbornadiene as well as spiropyran derivatives with TEMPO radical substituents were prepared and their light-induced structural changes to the corresponding quadricyclanes or merocyanine dyes and reverse reactions to the starting materials were investigated. While the intermolecular magnetic interactions tend to be preserved in norbornadiene–quadricyclane systems in spite of the differences of their Weiss temperatures, a switching of the intermolecular magnetic interactions was observed in the spiropyran–merocyanine systems.

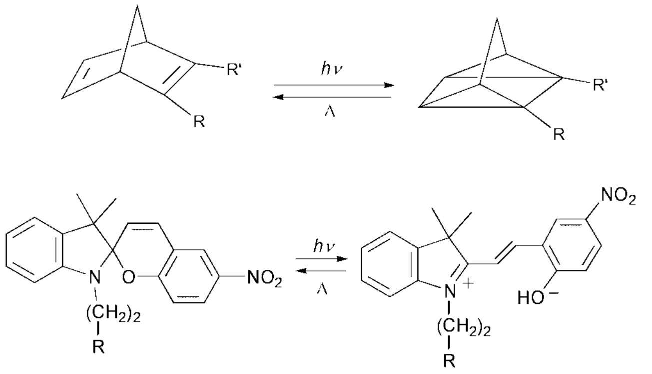
Introduction

It is of growing interest to develop photo-tunable spin systems and successful studies in this field have recently been reported for several inorganic compounds[1] and metal complexes[2] that show spin cross-over behaviour.[3] Despite the potential versatility of organic compounds to form such systems, no notable study of a purely organic system had been reported until very recently. It was only two years ago that the first experimental results were reported by Iwamura *et al.* in an azobenzene derivative bearing two aminoxyl radicals where changes to its UV and EPR spectra were observed upon irradiation.[4] More recently, Matsuda and Irie have succeeded in switching the intramolecular magnetic interactions upon irradiation in their diarylethene derivative bearing two nitronyl aminoxyls although the intermolecular interactions observed in each species are antiferromagnetic.[5]

In the course of our studies to develop new organomagnetic materials,[6] we have been interested in preparing organomagnetic compounds with multi-functionality, *e.g.*, organomagnetic conductors,[7] organomagnetic liquid crystals[8] and so forth. We have also been interested in developing photo-responsive organomagnets and with this aim have prepared systems such as norbornadienes[9] or spiropyrans[10] carrying aminoxyls. We report in this paper the preparation of two types of photo-responsive spin systems with aminoxyl radicals, *i.e.*, norbornadienes and spiropyrans carrying TEMPO radical substituents, their photo-responsive properties affording the corresponding quadricyclenes and merocyanine dyes and their backward reactions together with their magnetic behaviours based on the structural changes.[11]

Results and discussion

Preparation and photochemical properties of norbornadienes–quadricyclanes with TEMPO radical substituents



First, we examined the structural change from the amide derivative of norbornadiene with a TEMPO substituent to the corresponding quadricyclane (**Ia**–**Ib**, see below) by MM2 calculations. The bond angle around the carbon atom bearing the substituent in **Ia** was expected to change about 10° by the valence isomerization to **Ib** owing to the change of hybridization of the carbon atom from sp^2 to sp^3 (Fig. 1).[12] A change of magnetic properties, especially solid-state magnetic properties, was anticipated because it is not unusual for a slight structural change or modification in a molecule to cause a drastic change to its magnetic property in the solid state.

The preparation of the mono-TEMPO-substituted derivative of norbornadiene (**Ia**) was carried out as shown in Scheme 1 from cyclopentadiene **1** and propiolic acid **2a** through the carboxylic acid derivative **3a**. The acid was then derivatized with 4-amino-TEMPO to give the desired nobornadiene **Ia** although in low yield (24%, 2 steps). In a similar manner, the bis-TEMPO-substituted derivatives **IIa** and **IIIa** were prepared from the known diacid **3b**[13] by derivatizing with 4-amino- or 4-hydroxy-TEMPO.

The valence isomerizations from the norbornadienes to the corresponding quadricyclanes were found to occur by irradiation with light of 254 nm for several days in benzene solution and fortunately the radical centres were found to persist in the reactions during irradiation without damage being apparent from EPR data. A single crystal of the quadricyclane **Ib** was obtained by recrystallization from n-hexane–benzene solution and the molecular structure of **Ib** determined by X-ray analysis is shown in Fig. 2. The X-ray data are summarized in Table 1 together with selected bond lengths. The N–O (N1–O1) bond distance of the radical centre has been found from the analysis to be 1.28 Å; a normal value for an aminoxyl radical.[14] The bond angle between bridge-head carbon (C4′), the carbon atom carrying substituent (C5′) and the carbonyl carbon (C8′) is

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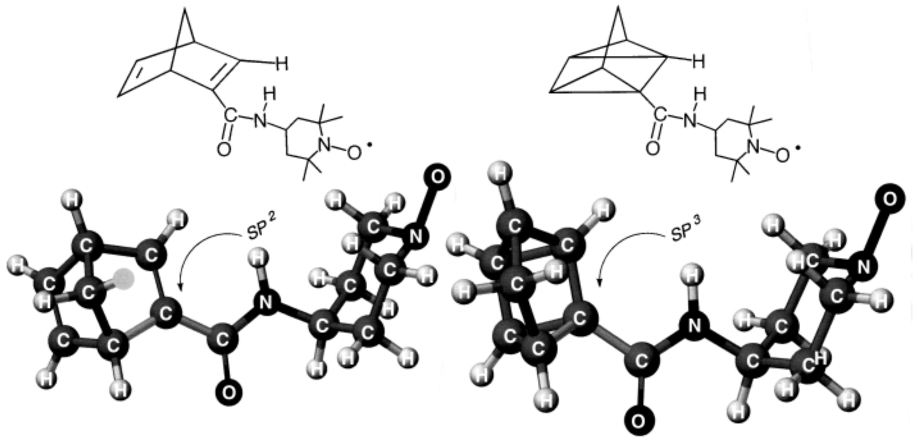
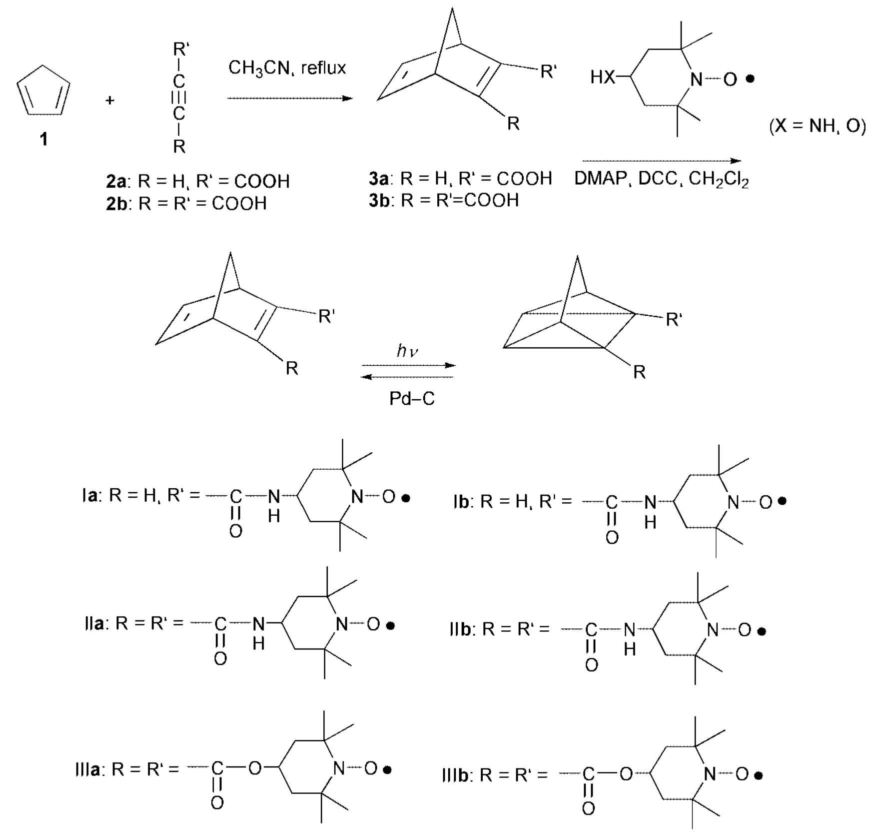


Fig. 1 Molecular structure of norbornadiene **Ia** (left) and quadricyclane **Ib** (right) by MM calculation.



Scheme 1

122.8° which is about 7° larger than the estimated angle by MM2 calculation.[12,15] The bond distances and angles found in the quadricyclane moiety of this compound are not unusual for this class of strained ring system.[16]

The backward reactions were catalyzed by Pd–C in ethyl acetate to give the starting materials in moderate isolated yields. The valence isomerization reactions could be easily monitored from the absorption spectral change as shown in Fig. 3 for the bis-amide derivatives as an example. Thus, the absorption maximum of 243 nm for **IIa** in acetonitrile solution shifts to 234 nm for **IIb** and *vice versa*. Similar spectrophotometric behaviour was observed in other valence isomers.

Preparation and photochemical properties of spiropyrans–merocyanines with TEMPO radical substituents

From the MM calculations for a TEMPO-substituted amide derivative of spiropyran **IVa** and the corresponding merocyanine **IVb**, relatively large differences in their molecular structures were anticipated and such structural changes were expected to cause the differences between their crystal and solid-state structures and hence magnetic properties.

The spiropyran derivatives **IVa** and **Va** were prepared following Scheme 2 from 2,3,3-trimethyl-3*H*-indole with 3-iodopropionic acid through the propionic acid derivative,[17] which then was derivatized with 4-amino- or 4-hydroxy-TEMPO to give **IVa** or **Va**. Irradiation of the spiropyrans in a non-polar solvent such as CCl_4 with light of 365 nm gave the reddish colored precipitates of the corresponding merocyanines **IVb** and **Vb** and thus these merocyanines could be isolated in the solid state.[18] On the other hand, on standing the merocyanines in a polar solvent such as acetonitrile or MeOH in the dark, the backward reactions were found to occur gradually to give the starting spiropyrans and thus the photochromic properties were actually observed in these systems.

The changes in the absorption spectra of the photochromic ester derivatives (**Va** and **Vb**) in acetonitrile are shown in Fig. 4. Thus, the absorption maxima of the starting material **Va** at around 341 nm shifts to the absorption maxima of the merocyanine **Vb** at around 409 nm and the absorption maxima of **Vb** goes back to 341 nm on standing in the solution. The kinetics of the backward reactions, which partially reflect the photochromic property in solution,[19] were investigated and the data are summarized in Table 2. The hypsochromic effects were observed in methanol solution compared with acetonitrile solution for both **IVb** and **Vb** and a larger lability was found in the acetonitrile solution compared with the methanol solution; this was estimated from the values of their half lives and the first-order reaction rates. As regards the relative lability between **IVb** and **Vb**, the amide derivative **IVb** was found to have appreciably larger lability compared with the ester derivative **Vb** as also shown in Table 2.

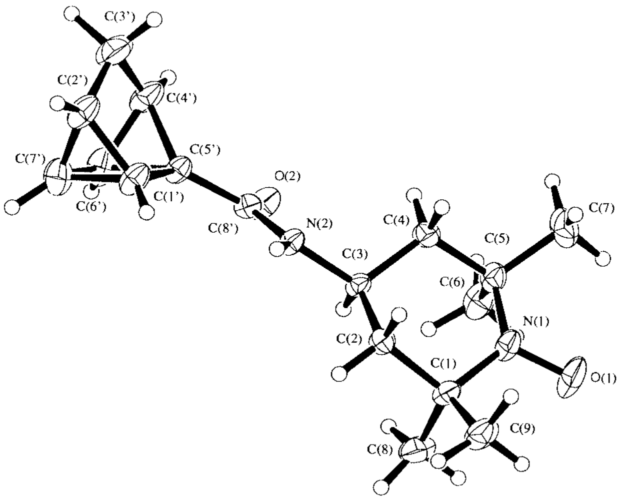


Fig. 2 Molecular structure of quadricyclane **Ib** by X-ray analysis.

Magnetic properties of norbornadienes–quadricyclanes

Typical triplet absorptions due to the isolated aminoxyl radical were observed in the EPR spectra of **Ia** and **Ib** as well as **IIa** and **IIb** in solution, whereas quintet-like absorptions were observed in the valence isomers **IIIa** and **IIIb**, suggesting the existence of intramolecular spin–spin interactions in the latter biradical systems. We then tried to estimate the magnitude of zero-field splitting parameters between the spin centres by low temperature EPR measurements in a 2-methyltetrahydrofuran matrix and the results are summarized in Table 3 together with the distances between the spin centres estimated by point dipole approximation. The results clearly suggest larger interactions in bis-esters (**IIIa** and **IIIb**) than bis-

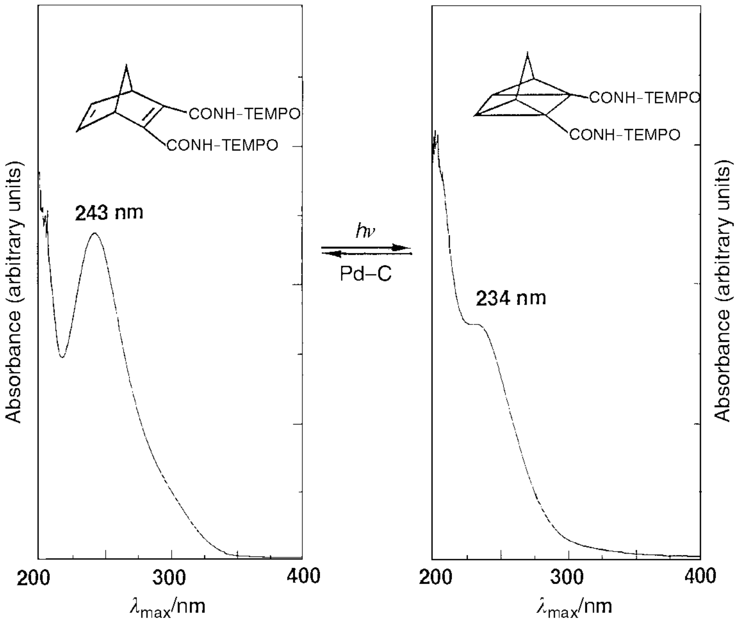
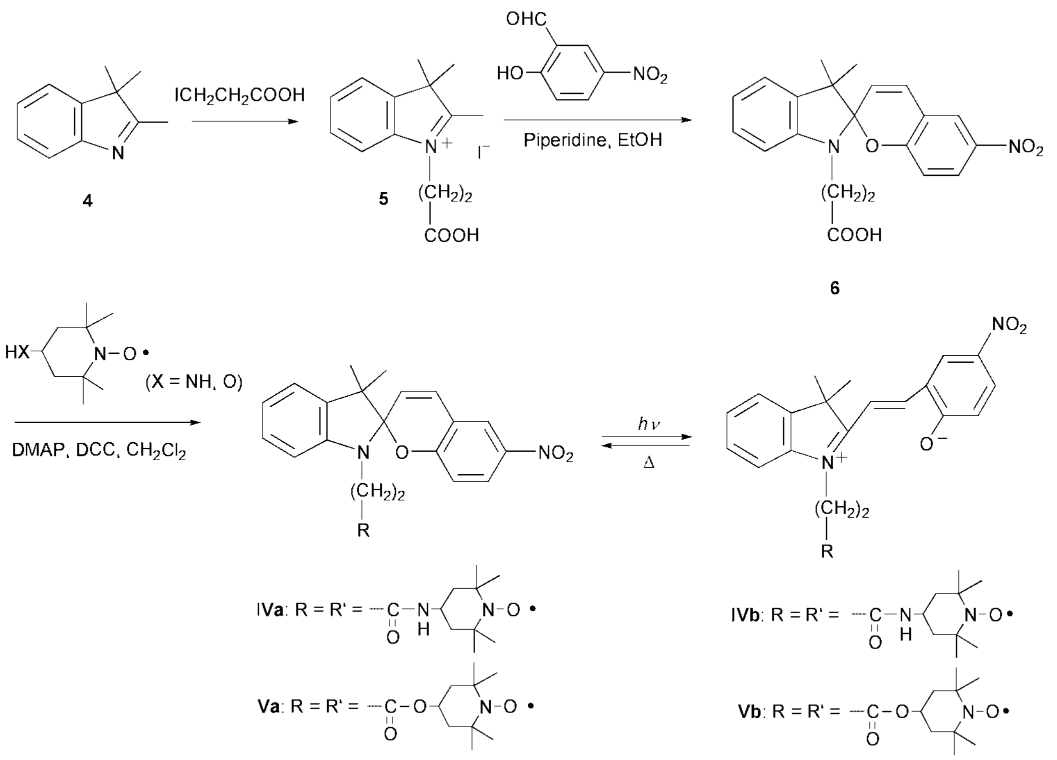


Fig. 3 Absorption spectra of norbornadiene **IIa** (left) and the corresponding quadricyclene **IIb** (right) in CH_3CN.

Table 1 Summary of crystal data and selected bond lengths for **Ib**

Crystal data		Atom 1	Atom 2	Bond length/Å
Formula	$C_{17}H_{25}N_2O_2$	O1	N1	1.281(3)
Formula weight	289.40	N1	C1	1.500(3)
Crystal system	Monoclinic	C1	C2	1.535(3)
Space group	$P2_1/c$	C2	C3	1.503(3)
a/Å	7.5297(3)	C3	N2	1.464(3)
b/Å	22.131(3)	N2	C8′	1.340(3)
c/Å	9.9543(6)	C8′	O2	1.239(3)
β/°	105.622(2)	C8′	C5′	1.471(3)
V/Å^3	1597.5(2)	C5′	C1′	1.523(4)
Z	4	C1′	C2′	1.500(4)
D_c/g cm^{-3}	1.203	C2′	C3′	1.486(4)
2θmax/°	55.3	C3′	C4′	1.508(4)
No. reflections measured	1195	C4′	C5′	1.523(4)
No. of reflections used in refinement $F > 3\sigma$	2497	C5′	C6′	1.523(4)
R	0.084	C6′	C7′	1.519(4)
R_W	0.161	C7′	C1′	1.526(4)



Scheme 2

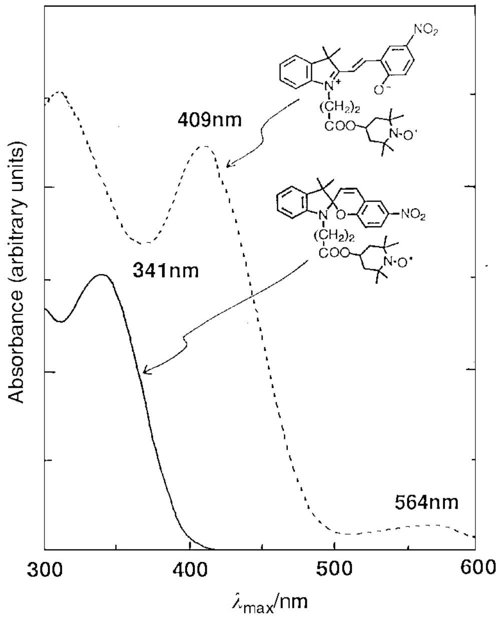


Fig. 4 Absorption spectra of spiropyran **Va** (solid line) and the corresponding merocyanine **Vb** (broken line) in CH_3CN.

Table 2 Photochromic properties of spiropyran derivatives

Comp.	Solvent	λ_{max}/nm	$t_{1/2}$/min	k[a]/s^{-1}
IVb	CH_3CN	554	35	3.30×10^{-4}
IVb	MeOH	540	150	7.70×10^{-5}
Vb	CH_3CN	564	25	4.62×10^{-4}
Vb	MeOH	537	137	8.43×10^{-5}

[a] First-order reaction rate from **IVb** to **IVa** or **Vb** to **Va**.

Table 3 EPR data of the norbornadiene–quadricyclane systems[a]

Compound	|D|/mT	|E|/mT	r/Å
IIa	4.20	0.96	8.73
IIb	4.22	0.91	8.71
IIIa	4.92	0.89	8.28
IIIb	4.86	0.92	8.31

[a] In 2-methyltetrahydrofuran at −150 °C.

amides (**IIa** and **IIb**), but so far as the valence isomers are concerned, no appreciable differences were apparent within the isomers.

The magnetic susceptibility measurements were carried out on polycrystalline samples using a SQUID susceptometer in the temperature range of 2–300 K. The temperature dependence data of χT values, as shown in Fig. 5(a), shows that antiferromagnetic intermolecular spin–spin interactions occur in the norbornadiene derivative **Ia**. However, a similar antiferromagnetic magnetic behaviour was observed in the corresponding quadricyclane derivative **Ib** in spite of the differences of their Weiss temperatures (Fig. 5(b)). The crystal structure of the latter compound viewed along *c*-axis is shown in Fig. 6. The molecules have been found to stack along the *c*-axis in a head-to-tail and staggered manner. The nearest intermolecular O–O distances are shown in dotted lines and amount to 4.21 Å, which are rather far apart for strong spin–spin interactions but are relevant to the antiferromagnetic behaviour found in this compound.

In addition, similar magnetic behaviour was observed in both bis-amide-substituted valence isomers **IIa** and **IIb** showing weak antiferromagnetic interactions in the lower temperature region. Rather unusual magnetic behaviour was found in bis-ester-substituted norbornadiene **IIIa**. Thus, the χT values decrease gradually along with a decrease in temperature indicating the predominance of the intramolecular antiferromagnetic interactions in the higher temperature region but which seems to be surpassed by intermolecular ferromagnetic interactions in the lower temperature region. However, so far as a comparison of valence isomers **IIIa** and **IIIb** is concerned, no large differences between magnetic behaviours have been found. The magnetic data in the solid state are summarized in Table 4. So far as we have examined, there is a tendency to preserve the magnetic behaviour in these valence isomers in spite of the differences of their Weiss temperatures although it is known

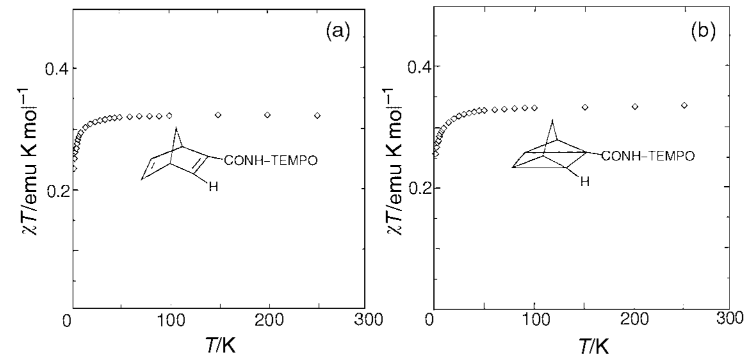


Fig. 5 (a) Temperature dependence of χT values of norbornadiene **Ia**. (b) Temperature dependence of χT values of quadricyclane **Ib**.

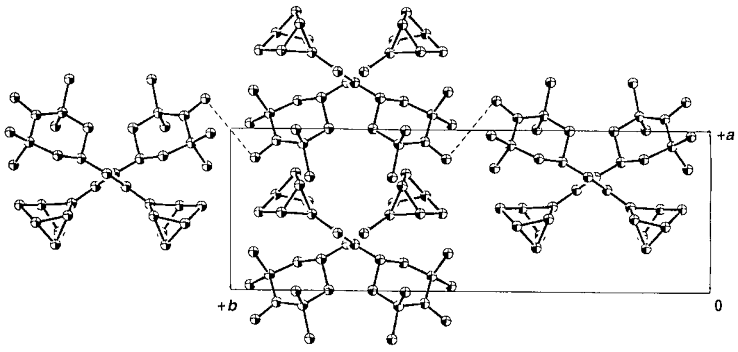


Fig. 6 Crystal structure of quadricyclane **Ib** viewed along the *c*-axis. Hydrogen atoms are deleted for simplification.

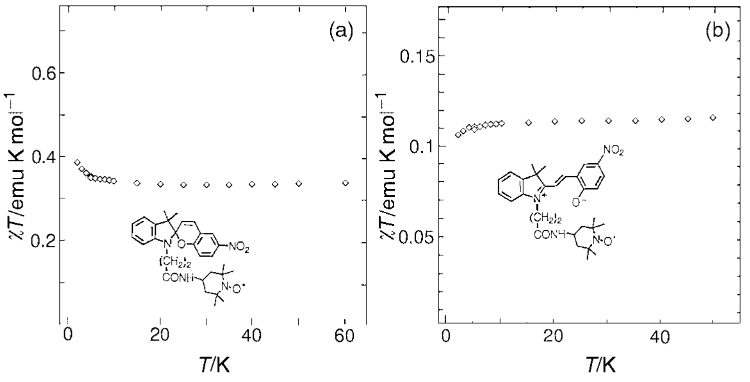


Fig. 7 (a) Temperature dependence of χT values of spiropyran **IVa** in the low temperature region, (b) Temperature dependence of χT values of mecrocyanine **IVb** in the low temperature region.

Table 4 Magnetic data of norbornadiene–quadricyclane systems

Comp.	Magnetic interaction	Weiss *T*/K[a]
Ia	Antiferromagnetic	−0.58
Ib	Antiferromagnetic	−0.33
IIa	Antiferromagnetic	−0.64
IIb	Antiferromagnetic	−0.68
IIIa	Ferromagnetic[b]	0.13
IIIb	Ferromagnetic[b]	0.09

[a] Fitting the Curie–Weiss rule. [b] In the lower temperature region (see text).

that magnetic interactions are sensitive to molecular change in general.

Magnetic properties of spiropyrans–merocyanines

In sharp contrast to the norbornadiene–quadricyclane systems examined, clear differences were observed in the magnetic properties in the solid state of spiropyran–merocyanine systems with a TEMPO radical substituent, although there were no appreciable differences in their EPR spectra in benzene solution for either pair (**IVa** and **IVb**; **Va** and **Vb**). Thus, the intermolecular spin–spin interactions observed in the low temperature region of **IVa** were found to be ferromagnetic with a Weiss temperature of 0.38 K (Fig. 7(a)), whereas the interactions in the corresponding merocyanine derivative **IVb** were found to be antiferromagnetic with a Weiss temperature of −0.82 K (Fig. 7(b)).[20]

Similarly, the ferromagnetic interactions found in the spiropyran derivative **Va** turn to antiferromagnetic in the corresponding merocyanine **Vb**. The solid state magnetic data are summarized in Table 5. Thus, it is suggested from the results that switching of the magnetic properties is possible in spiropyran systems carrying a TEMPO radical substituent, although the unstable nature of **IVb** and **Vb** in solution as well as in the solid state hampers further repetition of the forward and backward reaction. The differences between the magnetic properties observed in the spiropyran–merocyanine systems are supposed to be derived from differences in packing features in the crystals due to molecular structural differences. In spite of the limitation described above, to our knowledge, these are the first examples in a purely organic system in which the magnetic

Table 5 Magnetic data of spiropyran–merocyanine systems

Comp,	Magnetic interaction	Weiss T/K [a]
IVa	Ferromagnetic	0.38
IVb	Antiferromagnetic	−0.82
Va	Ferromagnetic	0.06
Vb	Antiferromagnetic	−0.15

[a] Fitting the Curie–Weiss rule.

interactions can be switched *in an intermolecular manner* through the structural changes invoked by light and heat.

Conclusion

We have developed two types of photo-responsive spin systems with aminoxyl radicals, norbornadienes and spiropyrans carrying TEMPO radical substituents and studied their structural change to the corresponding isomers together with their magnetic behaviour. In the norbornadiene–quadricyclane systems examined, the magnetic behaviours tend to be preserved within the systems, while in the spiropyran–merocyanine systems, the switching of intermolecular magnetic interactions was found to be possible between the isomers and therefore the systems could provide the first examples of photo-tunable *intermolecular* magnetic interactions in a purely organic system.

Experimental

Materials

4-Amino- and 4-hydroxy-TEMPO radicals are commercially available (Tokyo Kasei Kogyo Co.) and were used without further purification.

Instrumentation

Melting points were measured on a Yamato MP-21 apparatus and are uncorrected. IR spectra were recorded on a Jasco Report-100 spectrometer. UV–visible spectra were obtained on Jasco Ubest-35 spectrometer. MS spectra were taken using a JEOL JMS-AX 505 mass spectrometer. EPR spectra were obtained on a JEOL JES-FE3XG spectrometer and each g-value was determined using an Mn^{2+}/MgO marker as internal standard. Photo-irradiation was performed with a lamp of UVP/UVG-54 for light of 254 nm and a UVP/UVL-56 for light of 365 nm.

Computational studies

All MM2 calculations described herein were carried out using the CAChe system and the optimized parameters of the compounds investigated were obtained in their minimum potentials.

Magnetic measurements

Susceptibility measurements were carried out on a Quantum Design MPMS-5 SQUID susceptometer using *ca.* 10 mg for each powdered sample at 0.5 T (5–300 K) or at 0.1 T (2–5 K) and the paramagnetic susceptibility data were obtained after subtracting the diamagnetic contributions obtained experimentally from the observed values.

X-Ray structure determination

X-Ray diffraction data were collected on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-Kα radiation at 0 °C. The structure was solved by direct methods and expanded using Fourier techniques. Crystal data are listed in Table 1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. CCDC reference number 188/258. See http://www.rsc.org/suppdata/p2/b0/001993n/ for crystallographic files in .cif format.

Preparation of TEMPO-substituted norbornadiene derivatives (Ia–IIIa)

A typical procedure is exemplified for **Ia** and is as follows. A stirred mixture of propiolic acid (200 mg, 2.86 mmol), cyclopentadiene (944 mg, 14.3 mmol) in dichloromethane (30 cm^3) was heated to reflux and heating was continued for 3 h. The resulting reaction mixture was concentrated *in vacuo* to give crude norboradienecarboxylic acid as a pale yellow oil which was dissolved again in dichloromethane (30 cm^3), reacted with 4-amino-TEMPO (587 mg, 3.43 mmol), DCC (707 mg, 3.43 mmol) and DMAP (418 mg, 3.43 mmol) by stirring at ambient temperature for 1 d. The resulting solution was concentrated *in vacuo* to give a pale orange oil, which was subjected to column chromatography on SiO_2 (*ca.* 20 g) using benzene–ether as eluent. Radical **Ia** was obtained from the fractions eluted by 80% ether–benzene as a pale orange solid (201 mg, 24%, 2 steps) which was recrystallized from n-hexane–benzene to give a pure sample as pale yellow microcrystals. Mp 39–40 °C; EPR (benzene): triplet, $g = 2.007$, $a_N = 1.55$ mT; m/z (EI-HRMS) Found: 289.1817. Calcd. for $C_{17}H_{25}O_2N_2$: 289.1916; Found: C, 70.33; H, 8.66; N, 9.61. $C_{17}H_{25}O_2N_2$ requires: C, 70.55; H, 8.71; N, 9.68%; ν_{max} (Nujol)/cm^{-1} 3200, 3175 (NH), 1625 (CO); λ_{max} (CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 228 (6920).

In a similar manner, **IIa** and **IIIa** were prepared and the data are as follows. **IIa**: pale orange crystals. Mp 189–191 °C (decomp.); EPR (benzene): triplet, $g = 2.007$, $a_N = 1.56$ mT; m/z (FAB-HRMS) Found: 486.3256. Calcd. for $C_{27}H_{42}O_4N_4$: 486.3206; Found: C, 66.24; H, 8.58; N, 10.98. $C_{27}H_{42}O_4N_4$ requires: C, 66.64; H, 8.70; N, 11.15%; ν_{max} (Nujol)/cm^{-1} 3370, 3180 (NH), 1700, 1640 (CO), 1620 (C=C); λ_{max} (CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 244 (8850). **IIIa**: pale orange crystals. Mp 144–146 °C (decomp.); EPR (benzene): quintet (see text); m/z (EI-HRMS) Found: 488.2873. Calcd. for $C_{27}H_{40}O_6N_2$: 488.2886; Found: C, 66.77; H, 8.09; N, 5.82. $C_{27}H_{40}O_6N_2$ requires: C, 66.37; H, 8.25; N, 5.73%; ν_{max} (Nujol)/cm^{-1} 1725, 1700 (CO), 1625 (C=C); λ_{max} (CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 237 (8620).

Preparation of TEMPO-substituted quadricyclane derivatives (Ib–IIIb)

A benzene solution (50 cm^3) of **Ia** (100 mg, 0.35 mmol) was irradiated with light of 254 nm for 6 d and the reaction was monitored by TLC (SiO_2) during this period. After completion of the reaction, the solvent was evaporated and the crude product was purified by column chromatography on SiO_2 (*ca.* 20 g) using ether as eluent to give quadricyclane **Ib** as colorless solid (36 mg, 36%) which was recrystallized from n-hexane–benzene to give a pure sample as colorless plates. Mp 157–159 °C; EPR (benzene): triplet, $g = 2.007$, $a_N = 1.55$ mT; m/z (EI-HRMS) Found: 289.1853. Calcd. for $C_{17}H_{25}O_2N_2$: 289.1916; Found: C, 70.08; H, 8.57; N, 9.65. $C_{17}H_{25}O_2N_2$ requires: C, 70.55; H, 8.71; N, 9.68%; ν_{max} (Nujol)/cm^{-1} 2200, 2180 (CN); λ_{max} (CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 753 (16000), 855 (32800).

In a similar manner, **IIb** and **IIIb** were prepared and the data are as follows. **IIb**: pale orange crystals. Mp 198–200 °C (decomp.); EPR (benzene): triplet, $g = 2.007$, $a_N = 1.56$ mT; m/z (FAB-HRMS) Found: 486.3242. Calcd. for $C_{27}H_{42}O_4N_4$: 486.3206; Found: C, 66.44; H, 8.65; N, 11.41. $C_{27}H_{42}O_4N_4$ requires: C, 66.64; H, 8.70; N, 11.15%; ν_{max} (Nujol)/cm^{-1} 3360, 3190 (NH), 1690, 1660 (CO), 1625 (C=C); λ_{max} (CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 214 (6480). **IIIb**: pale orange crystals. Mp 149–150 °C (decomp.); EPR (benzene): quintet (see text); m/z (EI-HRMS) Found: 488.2891. Calcd. for $C_{27}H_{40}O_6N_2$ 488.2886;

Found: C, 66.38; H, 8.20 N, 5.72. $C_{27}H_{40}O_6N_2$ requires: C, 66.37; H, 8.25; N, 5.73%; ν_{max} (Nujol)/cm^{-1} 1720, 1700 (CO); λ_{max} (CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 217 (7180).

The backward reaction from quadricyclanes (Ib–IIIb) to norbornadienes (Ia–IIIa)

To a stirred solution of **Ib** 20 mg (0.069 mmol) in ethyl acetate (20 cm^3) was added a catalytic amount of Pd–C (10%) and the reaction mixture was heated (80 °C) for 2 h. After evaporation of the solvent, the crude product was purified by SiO_2 (*ca.* 10 g) using ether as eluent to give 19 mg of **Ia** (95%) which was identified by TLC, mp and UV measurement. In a similar manner, **IIb** and **IIIb** were reverted to the corresponding **IIa** and **IIIa** in 95% and 40% yield, respectively.

Preparation of TEMPO-substituted spiropyran derivatives (IVa and Va)

A typical procedure is exemplified for **IVa** and is as follows. To a stirred solution of the acid **6** 708 mg (2.05 mmol) in dichloromethane (30 cm^3) was added 4-amino-TEMPO 394 mg (2.30 mmol), DCC 495 mg (2.40 mmol) and DMAP (275 mg, 2.10 mmol) by stirring at ambient temperature for 1 d. The resulting solution was concentrated *in vacuo* to give a pale yellow solid as the crude product, which was purified by column chromatography on SiO_2 (*ca.* 20g) using benzene–ether as eluent. Radical **IVa** was obtained from the fractions eluted by (1 : 1) ether–benzene as a pale yellow solid (679 mg, 62%) which was recrystallized from ethyl acetate to give pure yellow microcrystals. Mp 185–187 °C; EPR (benzene): triplet, $g = 2.007$, $a_N = 1.57$ mT; *m/z* (FAB-HRMS) Found: 533.2914. Calcd. for $C_{30}H_{37}O_5N_4$: 533.2842; Found: C, 67.52; H, 6.75; N, 10.36. $C_{30}H_{37}O_5N_4$ requires: C, 67.81; H, 6.99; N, 10.36%; ν_{max} (Nujol)/cm^{-1} 3425, 3290 (NH), 1665, 1650 (CO), 1610 (C=C); λ_{max} (CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 266 (17100), 341 (8160).

In a similar manner, **Va** was prepared and the data are as follows: pale yellow microcrystals. Mp 187–189 °C; EPR (benzene): triplet, $g = 2.007$, $a_N = 1.56$ mT; *m/z* (FAB-HRMS) Found: 534.2667. Calcd. for $C_{30}H_{36}O_6N_3$: 534.2683; Found: C, 67.12; H, 6.78; N, 7.83. $C_{30}H_{36}O_6N_3$ requires: C, 67.40; H, 6.79; N, 7.86%; ν_{max} (Nujol)/cm^{-1} 1730 (CO), 1605 (C=C); λ_{max} (CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 267 (18500), 341 (9640).

Preparation of TEMPO-substituted merocyanine derivatives (IVb and Vb)

Spiropyran derivative **IVa** 100 mg (0.19 mmol) was dissolved in CCl_4 (100 cm^3) and the solution was irradiated with light of 365 nm for 5 d. During the irradiation, the colour of the solution turned from pale yellow to reddish violet and a coloured precipitate was gradually formed. The precipitate was filtered by suction, washed well with CCl_4 and dried under reduced pressure to give **IVb** (43 mg, 33%) as a reddish brown powder. The filtrate was further irradiated for 2 d to give additional formation of **IVb** (12 mg, 9%). Mp >164 °C (decomp.); EPR (benzene): triplet, $g = 2.006$, a_N=1.53 mT; *m/z* (FAB-HRMS) Found: 533.2901. Calcd. for $C_{30}H_{37}O_5N_4$: 533.2842; Found: C, 53.72; H, 5.94; N, 7.97. $C_{30}H_{37}O_5N_4 \cdot CCl_4$ requires: C, 54.16; H, 5.43; N, 8.15%; ν_{max} (Nujol)/cm^{-1} 3450–3220br (NH), 1650 (CO), 1600 (C=C); λ_{max} (CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 246 (11800), 400 (5130), 556 (530).

In a similar manner, **Vb** was prepared and the data are as follows: reddish brown powder. Mp >154 °C (decomp.); EPR (benzene): triplet, $g = 2.007$, $a_N = 1.56$ mT; *m/z* (FAB-HRMS) Found: 534.2731. Calcd. for $C_{30}H_{36}O_6N_3$: 534.2683; Found: C, 53.56; H, 5.73; N, 5.93. $C_{30}H_{36}O_6N_3 \cdot CCl_4$ requires: C, 54.08; H, 5.27; N, 6.10%; ν_{max} (Nujol)/cm^{-1} 1730 (CO), 1600 (C=C); λ_{max} (CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 245 (8990), 301 (7560), 405 (5650), 564 (460).

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12 At first, the MM2 calculation was carried out with no information of X-ray data to give the results described in text. However, when the X-ray data of **Ib** (space group, lattice parameters, atomic coordinates, *etc.*) was taken into account, closer values to the observed data for **Ib** were obtained. For example, the bond angle around (C5′), *i.e.*, (C4′)–(C5′)–(C8′) was calculated to be 125.3°, which is a slightly larger value than the observed one. We thank a referee for a helpful comment on this point.

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