JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Photoswitchable Intramolecular Through-Space Magnetic Interaction

Jiaobing Wang, Lili Hou, Wesley R. Browne, and Ben L. Feringa*

Centre for Systems Chemistry, Stratingh Institute for Chemistry, and Zernike Institute for Advanced Materials,
University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

S Supporting Information

ABSTRACT: The interaction between two TEMPO spin centers connected to a photoswitchable overcrowded alkene changes from noncoupled (three-line EPR spectrum) in the trans state, where the two spin centers are separated by ∼22 Å, to strongly coupled (five-line EPR spectrum) in the cis state, where the separation is ∼7 Å, upon photoswitching. Importantly, the performance of the alkene switching unit is essentially unaffected by the spin centers.

Dynamic photocontrol over the magnetic interaction between stable organic radical centers (RCs) is a promising strategy for molecular-scale information processing and memory devices.[1,2] Several photochromic units (PUs), such as azobenzenes,[3] diarylethenes,[4] and Schiff bases,[5] have been functionalized with free RCs to construct systems in which photoswitching of the PU typically modulates the through-bond interaction of the RCs, producing a readable magnetic signal. Irie and co-workers[4] have reported an impressive series of RC−PU−RC compounds in which reversible photocyclization of the diarylethene PU can switch a through-bond spin−spin coupling of pairs of nitronyl nitroxide RCs on and off, as manifested by substantial changes in the electron paramagnetic resonance (EPR) spectra. However, in these π-conjugated RC−PU−RC systems, modulation of the chain length of the π delocalization by photoisomerization of the PU was used to control the spin−spin interaction. Nevertheless, achieving a system that operates by on/off switching of the electronic interaction between the RC units mediated through the π system of the PU unit without compromising the efficiency of the photoswitching processes is a challenging task that requires careful optimization of the π-conjugated structures.[4a]

Here we present a highly efficient photoswitchable magnetic system by which intramolecular through-space magnetic interactions between two RCs can be switched on and off reversibly. The molecular design, which does not rely on through-bond interactions between the RCs, avoids loss of photochemical performance. In this system (Figure 1), the RC−PU−RC functional subunits are connected in a non-π-conjugated manner via alkylamide spacers to minimize the electronic interference between the PU and RC units. The switching unit (see *trans*-**1**) is based on the well-known overcrowded alkenes (OA),[6] to which a pair of stable 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radicals are attached via amide bonds. Light-driven cis−trans isomerization of the OA unit can switch the through-space magnetic interactions between the two TEMPO radicals. In the trans state, the TEMPO units are kept apart, and the three-line EPR spectrum is assigned as that of a monomer-like TEMPO unit. In stark contrast, in the cis state, the two TEMPO units are in sufficient proximity to allow for strong spin−spin coupling, as manifested by a five-line EPR spectrum. These two states can be interconverted by alternate irradiation at λ_{irr} = 312 and 365 nm at room temperature in several solvents.

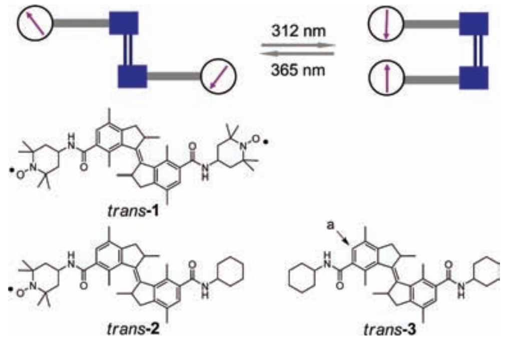

Figure 1. Representation of the photoswitching of intramolecular through-space magnetic interaction and the structures of *trans*-**1**−**3**.

Detailed synthesis procedures and characterization data for *trans*-**1** and the reference compounds *trans*-**2** and *trans*-**3** are provided in the Supporting Information (SI). Mono-TEMPO-substituted *trans*-**2** was prepared to confirm the intramolecular nature of the photoswitchable spin−spin coupling observed for *trans*/*cis*-**1**. Bis(cyclohexylamine)-substituted *trans*-**3**, which does not bear RCs, was used for comparison.

Compounds *trans*-**1**−**3** display similar UV−vis absorption spectra (Figure 2 and Figure S1 in the SI) with a maximum centered at 297 nm that is ascribed to absorption by the *trans*-OA unit. Irradiation at 312 nm resulted in a decrease in the absorption of *trans*-**1** at 297 nm with a concomitant increase of a new absorption band at 350 nm (Figure 2a). An isosbestic point was maintained at 319 nm over the course of the irradiation. At the photostationary state (PSS), an 89% yield of *cis*-**1** was formed. Compounds *trans*-**1**−**3** exhibited essentially identical changes in their absorption spectra upon irradiation at 312 nm. The spectral changes are assigned to the trans → cis photoswitching of the OA unit.[6a,b] For the reference compound **3**, ^{1}H NMR spectroscopy was employed to monitor the photoswitching. The aromatic proton H_a shifted from 7.02 to 6.95 ppm (Figure S1), characteristic[6a,b] of the formation of *cis*-**3**.

The changes in the magnetic interaction between the two TEMPO radical units of compound **1** upon photoswitching were monitored by EPR spectroscopy (Figure 2b). A three-line spectrum (g = 2.006, A_N = 15.5 G) typical of TEMPO was observed for *trans*-**1**, indicating the absence of significant spin coupling be-

Received: March 30, 2011
Published: May 04, 2011

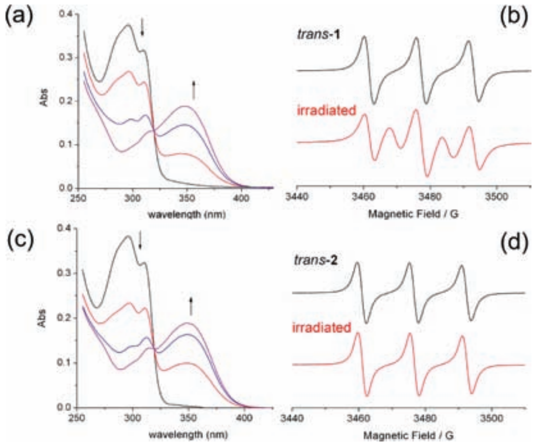

Figure 2. (a, c) UV−vis absorption (1.5×10^{-5} M) and (b, d) EPR (1.0×10^{-3} M) spectroscopy of (a, b) *trans*-**1** and (c, d) *trans*-**2** upon UV irradiation at 312 nm for 70 s in ethyl acetate at 20 °C. For fitted EPR spectra, see the SI.

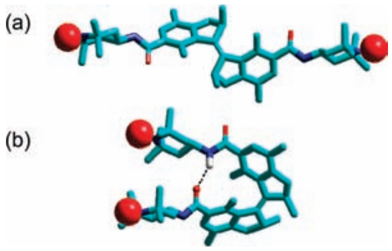

Figure 3. Energy-minimized structures of (a) *trans*-**1** and (b) *cis*-**1** optimized using DFT at the B3LYP/6-31G (d,p) level.

tween the two radicals.[7−10] The EPR spectra showed substantial changes from a three- to a five-line spectrum upon irradiation at 312 nm. The mixture of three- and five-line EPR signals observed at the PSS (>71% *cis*-**1**) was in agreement with the PSS determined by UV−vis absorption and ^{1}H NMR spectroscopy. The changes in the EPR spectrum upon switching to the cis state are indicative of coupling between the two TEMPO RCs, which is larger than the ^{14}N hyperfine coupling constant.[7] Density functional theory (DFT) molecular modeling studies at the B3LYP/6-31G* level (Figure 3) indicated that the two TEMPO radicals are in proximity in the cis state[11] with a separation between the N−O centers of ~7.1 Å, which coincides with the reported distance through which strong spin−spin interactions occur.[9] In contrast, in the trans state, the two TEMPO units are sufficiently isolated from each other (~22.4 Å) to preclude significant spin coupling. The EPR spectrum of the monosubstituted reference compound *trans*-**2** was unaltered (Figure 2d) upon photoisomerization of the OA unit (Figure 2c), supporting the assignment of intramolecular coupling in *cis*-**1**.

The photoswitching was reversible (Figure 4 and Figure S3). Irradiation at 365 nm drove the reverse cis → trans isomerization, with a decrease in the intensity of the absorption band at 350 nm (Figure S3a) and recovery of the initial absorption of *trans*-**1** at 297 nm (86% *trans*-**1** at the PSS). Concomitant recovery of the three-line EPR spectrum was also observed (Figure S3b).

An important feature of the present system is that the radical centers do not interfere with the photochemical properties of the switching unit. Comparison of the quantum yields for photoswitching of compounds **1**−**3** (Table 1) indicates that TEMPO functionalization did not significantly affect the isomerization process in either direction. This is a remarkable feature in view of the fact that orders-of-magnitude decreases in the quantum efficiency have been observed in π-conjugated RC−PU−RC systems.[4c] In addition, the intramolecular nature of the magnetic interaction in the current study, in contrast to those showing intermolecular interactions,[5] allows this dynamic system to operate under a wide range of experimental conditions. Photoisomerization resulted in substantial changes to the EPR spectrum in various solvents, including ethyl acetate, dichloromethane, toluene, and acetonitrile (Figure S4), even at micromolar concentrations (Figure S5).

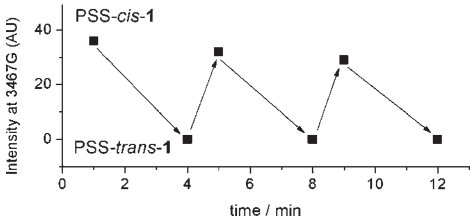

Figure 4. Reversibility of the photoswitching as followed by EPR spectroscopy upon alternate irradiation of PSS *cis/trans*-**1** at 365 and 312 nm, respectively.[12]

Table 1. Quantum Yields for Photoisomerization of Compounds 1−3

compound	Φ_{312}	Φ_{365}
1	0.131	0.023
2	0.136	0.029
3	0.148	0.038

In summary, the present system operates at room temperature and shows substantial changes in the RC−RC interaction with essentially complete retention of the photochemical performance of the overcrowded alkene switching unit.

■ ASSOCIATED CONTENT

S Supporting Information. Synthetic procedures and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

b.l.feringa@rug.nl

■ ACKNOWLEDGMENT

The Netherlands Organization for Scientific Research (NWO−CW) (Vidi Grant to W.R.B.) and the ERC (Advanced Investigator Grant 227897 to B.L.F.) are acknowledged for funding

■ REFERENCES

(1) Sato, O.; Tao, J.; Zhang, Y.-Z. *Angew. Chem., Int. Ed.* **2007**, *46*, 2152.

(2) Nakatsuji, S. *Chem. Soc. Rev.* **2004**, *33*, 348.

(3) An azobenzene-based dynamic magnetic system has been reported. However, a change in EPR signal was observable only for a preirradiated sample at the cryogenic temperature (10 K). See: Hamachi, K.; Matsuda, K.; Itoh, T.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2937.

(4) (a) Tanifuji, N.; Irie, M.; Matsuda, K. *J. Am. Chem. Soc.* **2005**, *127*, 13344. (b) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2001**, *123*, 9896. (c) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 7195. (d) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 8309.

(5) Ratera, I.; Ruiz-Molina, D.; Vidal-Gancedo, J.; Wurst, K.; Daro, N.; Létard, J.-F.; Rovira, C.; Veciana, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 919.

(6) (a) Pollard, M. M.; Meetsma, A.; Feringa, B. L. *Org. Biomol. Chem.* **2008**, *6*, 507. (b) Wang, J.; Kulago, A.; Browne, W. R.; Feringa, B. L. *J. Am. Chem. Soc.* **2010**, *132*, 4191. (c) Wang, J.; Feringa, B. L. *Science* **2011**, *331*, 1429. (d) Browne, W. R.; Feringa, B. L. *Nat. Nanotechnol.* **2006**, *1*, 25. (e) Feringa, B. L. *J. Org. Chem.* **2007**, *72*, 6635.

(7) Porel, M.; Ottaviani, M. F.; Jockusch, S.; Jayaraj, N.; Turro, N. J.; Ramamurthy, V. *Chem. Commun.* **2010**, *46*, 7736.

(8) Sartori, E.; Khudyakov, I. V.; Lei, X.; Turro, N. J. *J. Am. Chem. Soc.* **2007**, *129*, 7785.

(9) Bardelang, D.; Banaszak, K.; Karoui, H.; Rockenbauer, A.; Waite, M.; Udachin, K.; Ripmeester, J. A.; Ratcliffe, C. I.; Ouari, O.; Tordo, P. *J. Am. Chem. Soc.* **2009**, *131*, 5402.

(10) Matsuda, K.; Stone, M. T.; Moore, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 11836.

(11) Molecular modeling studies suggested the presence of an intramolecular hydrogen bond between the amide groups in the cis state (Figure 3b) that cooperates with the OA platform to direct the two TEMPO arms in a proper orientation for spin−spin interaction. This conclusion was further supported by the experimental observation that the coupled EPR signal was less evident in a protic solvent such as ethanol than in an aprotic solvent such as THF (Figure S2).

(12) Upon extended irradiation, gradual degradation of the switching unit was observed, leading to a loss of reversibility. The instability is due to the presence of the amide linker unit and was observed for model compounds **2** and **3** also.