Recent progress toward the exploitation of organic radical compounds with photo-responsive magnetic properties

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Recent studies on the exploitation of novel organic radical compounds that exhibit photo-responsive properties by illumination are described in this *tutorial review*. Those so far reported consist of a variety of photo-responsive π-electron moieties such as azobenzene, diarylethene, biindenylidene, terphenoquinone, anthracene, naphthopyran, arylimine, or hexaarylbiimidazoles, bearing stable organic radicals or generating organic radicals as spin centres for magnetic properties. The switching behaviours of their magnetic properties evoked by the stimuli of irradiation are discussed by taking the associated structural changes into consideration.

1 Introduction

The dawn of photochromism[1] was glimpsed in the latter half of 19th century,[2,3] though, as might be expected, the term 'photochromism' was not in use at that time. The chemistry of organic radicals, on the other hand, virtually originated from the famous discovery of the triphenylmethyl radical reported by M. Gomberg in 1900,[4] some decades after the former discovery. Interestingly, almost at the same time with the discovery of the first radical, W. Marckward observed the color change of β-tetrachloro-1-ketodihydrona-phthalene on exposure to sunlight and reported it in 1899, naming the phenomena 'Phototropie' (Scheme 1).[5] However, the mecha-

Scheme 1
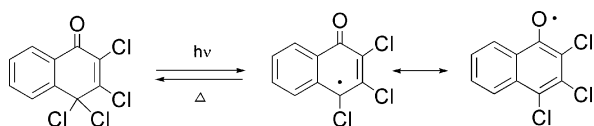
nism of the coloration was for long unknown until it was disclosed by G. Sheibe and F. Feichtmayr over 60 years later that the

Shin'ichi Nakatsuji was born in Ehime, Japan in 1949 and obtained a PhD in 1977 at Osaka University on the chemistry of dehydroannulenes under the supervision of Professor Masazumi Nakagawa. After studying as a JSPS postdoctoral fellow at the same university, he joined in 1978 the faculty of pharmaceutical sciences, Nagasaki University, as a research associate and worked with Professor Shuzo Akiyama in the field of dye chemistry and organic analytical reagents. He worked one year (1984–1985) at the TH Darmstadt with Professor Klaus Hafner as an Alexander von Humbodlt fellow. He was promoted to associate professor at Nagasaki University, and then in 1990 moved to the newly opened faculty of science in Hi-meji Institute of Technology and was appointed a professor in 1998. His main research interests are in the preparation of organic functional materials, especially organic magnetic materials and conductors, and novel π-electron systems.
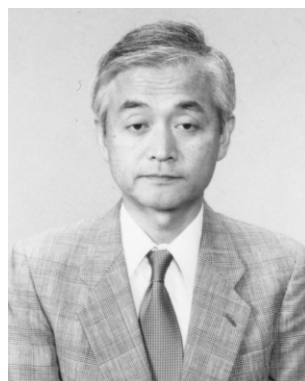
formation of a radical species (aroxyl radical) is the essential origin for the colour change.[6] Although it is quite probable that the combination of organic radicals and photochromism was not envisaged at that time around 1900, much attention is now, about a century later, focused on this combination owing to the remarkable progress with molecular-based materials including organic magnetic materials in recent years.[7]

Some six years ago, we predicted in an article about organic magnetic materials based on nitroxide (aminoxyl) radicals[8] that the development of novel magnetic materials with multi-functionality, *i.e.*, the development of novel magnetic materials which respond to light, heat, pressure, electricity or other stimulators would be a possible area for future investigation,[9] since they are interesting not only from the viewpoint of basic science but also in technological aspects, to afford examples of molecular devices as thermal or optical switching systems being correlated with spins. Whereas, at that time, several interesting examples of photo-responsive spin systems had been reported one after another in inorganic com-pounds[10] and metal complexes,[10–12] those of organic compounds remained still scarcely explored. Since that time, we have tried to prepare organic spin systems with photo-responsive properties and, meanwhile, several research groups have also investigated their own spin systems with photo-responsive properties independently. An organic radical compound with azobenzene moiety was reported by Iwamura, Matsuda *et al.* in 1998,[13] followed by the results of several research groups with various photo-responsive π-electron systems. We wish to survey in this tutorial review article the progress towards exploitation of organic radical compounds with photo-responsive magnetic properties predominantly devel-oped during the past decade by introducing the systems prepared by several research groups, including ours. Although there are some recent prominent examples of photo-responsive spin systems in which the spin sources do not originate from pure organic radicals but from metals, radical anion salts, or carbenes, these are not covered in this article and readers are recommended to consult the relevant references.[14–16] This article is confined to photo-respon-sive spin systems that do not have any metal-based spins in them. The systems include such photo-responsive π-electron moieties as azobenzene, diarylethene, biindenylidene, terphenoquinone, an-thracene, naphthopyran, arylimine, and hexaarylbiimidazoles, bearing stable organic radicals or generating organic radicals as spin centres. Actually, the systems with photo-responsive magnetic properties investigated in recent years are largely classified, depending on the kind of structural changes, into intramolecular or intermolecular ones (I and II) and, moreover, they are further categorized in the following manner; I (A): organic biradicals being associated with molecular structural change by irradiation and

dealing with the intramolecular magnetic interactions; I (B) organic biradicals being generated from the diamagnetic precursors by irradiation; I (C) organic high-spin multiplets being generated from antiferromagnetic radicals by irradiation; I (D) organic radical compounds being associated with molecular structural change by irradiation and dealing with the intermolecular magnetic interactions; II (A): organic radical compounds forming dimeric biradical compounds; and II (B): organic radical pairs being generated by homolysis of the corresponding diamagnetic precursors (Chart 1).
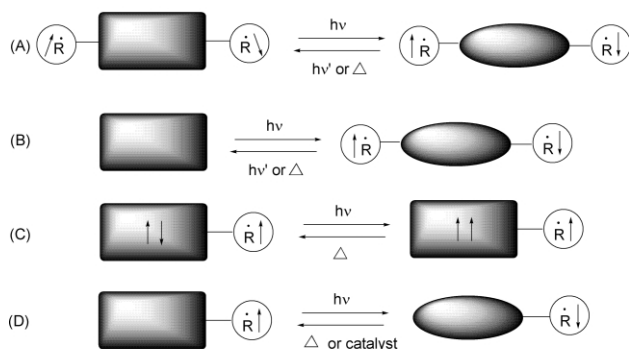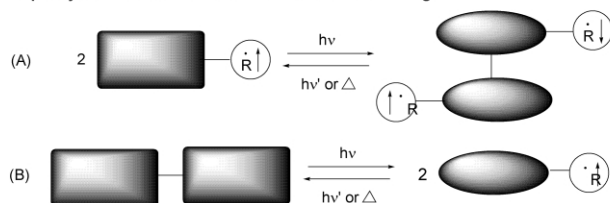

Chart 1

2 Organic photo-responsive radicals based on intramolecular structural change

Several organic radical compounds with photo-responsive properties that exhibit changes in their magnetic properties upon irradiation and that are based on *intramolecular structural change* will be discussed in this section.

2-1 Organic biradical compound with azobenzene unit

This first example is classified as type I (A). An azobenzene derivative **1a** with two nitronyl nitroxide radical substituents has been prepared through the diformyl derivative as an intermediate.[13] The *trans*-isomer thus prepared was then subjected to photo-irradiation in cyclohexane using 345–415 nm light with a Xe lamp to observe the corresponding *cis*-isomer **1b** in solution (Scheme 2), which could be clearly detected by the Uv-vis spectral change. When the irradiation was halted, the original peaks were found to be recovered albeit with less intensity. The alteration of EPR spectra due to the isomerization by irradiation was also observed at cryogenic temperature in toluene solution, although the conversion
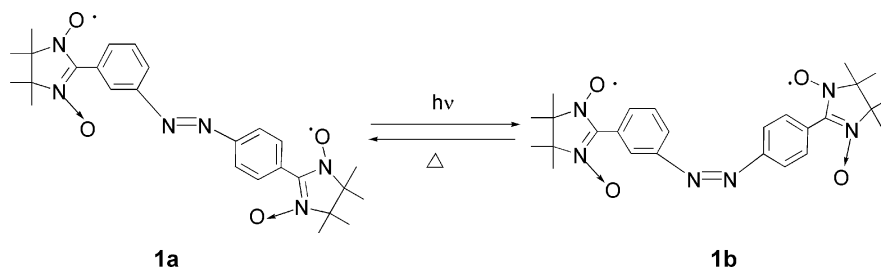
is also not complete in this case. Thus, the photo-responsive organic radical compound was successfully prepared, even if full conversion between the isomers is not completely attained.

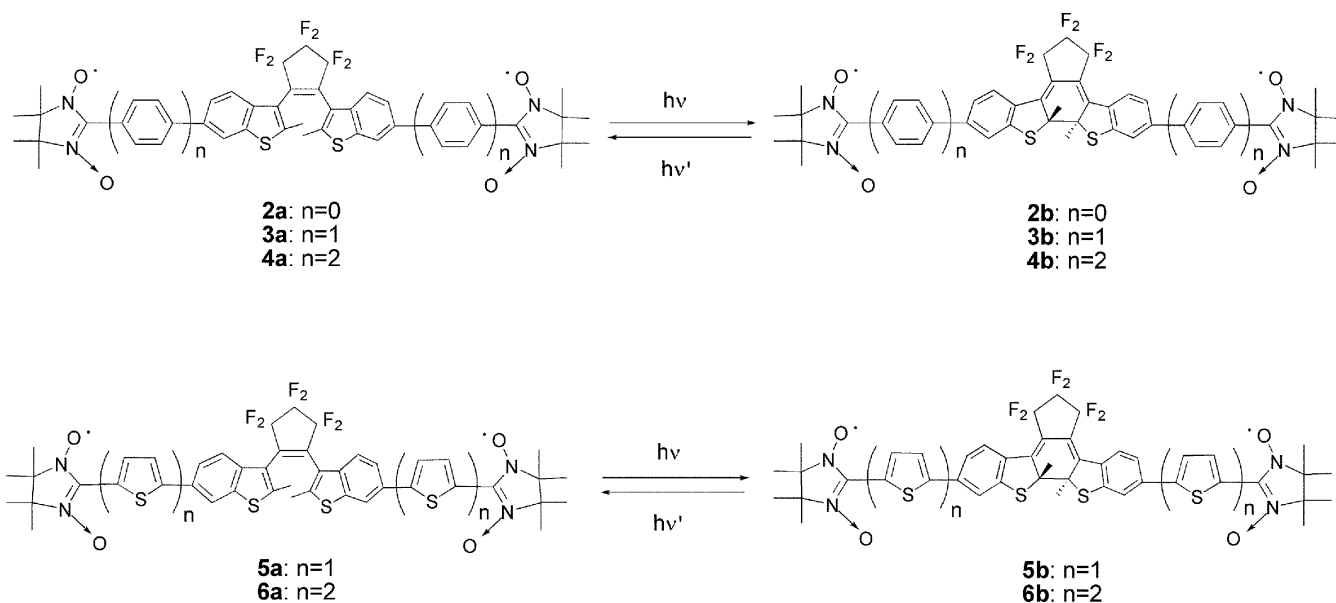### 2-2 Organic biradical compounds with diarylethene unit

The next examples are classified as type I (A) and, moreover, these have the additional functionality of switching effects (on and off) through conjugation (and non-conjugation) owing to the photo-chemical ring closure (and opening). A series of smart diarylethane derivatives with two nitronyl nitroxide substituents **2a–6a** has recently been prepared by Matsuda and Irie and show excellent photochemical conversions in all cases to the corresponding closed-ring isomers **2b–6b** (Scheme 3).[17–20] The backward reactions were also reported to occur by irradiation with light of suitable wavelength, giving the starting open-ring isomers in each case. Thus eminent photochromic systems could be constructed from these diarylethene derivatives.

Moreover, apparent switching properties of the *intramolecular magnetic interactions* have been impressively realized in each of the photochromic spin couplers. Thus, the magnitude of the intramolecular antiferromagnetic interaction of $2J/k_B = -2.2$ K (the state of switch off) between the spins in the open-ring isomer **2a** increases appreciably to the larger absolute value of $2J/k_B = -11.6$ K (the state of switch on) in the closed-ring isomer **2b** by the photochemical ring closure and *vice versa*.[17] Interestingly, the photoswitching of intramolecular magnetic interactions could be demonstrated between the spin couples **3a** and **3b** by means of EPR spectroscopy at room temperature, since the exchange interaction is comparable to the hyperfine coupling constant in **3a** ($|2J/g\mu_B| \doteqdot 8$ G, $|2J/k_B| \doteqdot 1 \times 10^{-3}$ K) by inserting a couple of benzene rings in **2a**, while that of the corresponding closed-ring isomer **3b** is much larger than the hyperfine coupling constant ($|2J/g\mu_B| > 600$ G, $|2J/k_B| > 0.08$ K). That is, the strength of exchange interaction was switched by more than 2 orders of magnitude in the spin couplers.[18] By incorporating *p*-phenylene spacers as in **4a** and **4b**, the intrinsic change of the exchange interactions between open- and closed-ring isomers was estimated to be more than 30-fold.[19] Although the photochromic reactivity of the diradical diarylethenes with oligothiophene spacers (**6a/6b**) was much reduced, the magnetic interaction between the spins through oligothiophene spacers was stronger than that through oligophenylene spacers and thus the difference of the exchange interaction between open- and closed-ring form isomers was estimated to be more than 150-fold.[20]
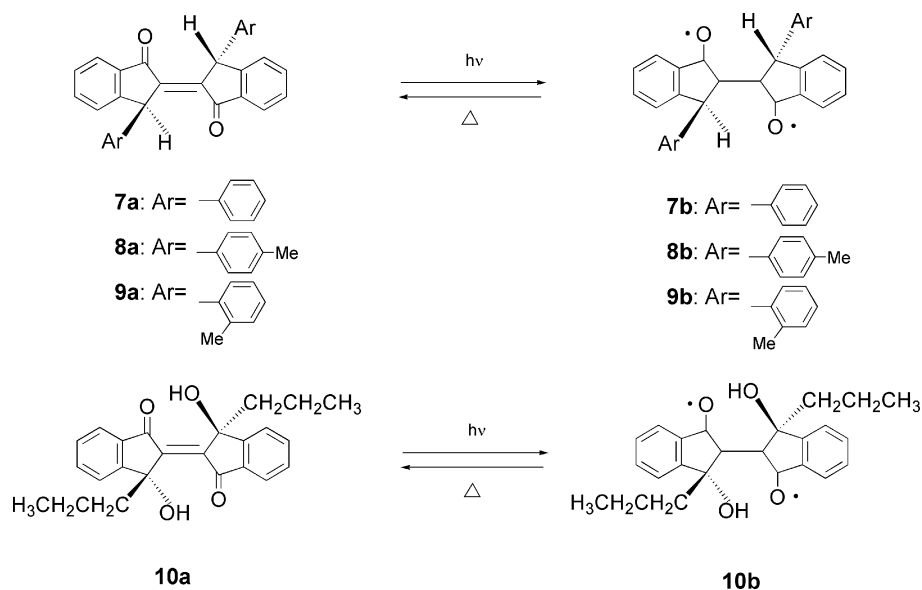
2-3 Organic biradical compounds with biindenylidene unit

These are examples of type I (B). Tanaka and Toda has recently developed intriguing photochromic biindenylidene derivatives **7a-9a**, each single crystal of which gave the corresponding reddish purple biradicals **7b-9b** on exposure to sunlight. The formation of the triplet biradicals was clearly ascertained by the analysis of EPR signals, that is, the zero field splitting parameters for **7b** are as follows; $D = 13.78$ G, $E = 1.377$ G, $g_{xx} = 2.0026$, $g_{yy} = 2.0027$, $g_{zz} = 2.0020$.[21] Heating the irradiated sample above 60 °C caused it to revert to yellow immediately, thus showing the reversible photochromic nature even in the crystal state (Scheme 4).

More recently, Meng *et al.* examined the photochromic properties of a biindenylidenedione **10a** and found that it afforded the

1a   **1b**

Scheme 2

2a: n=0
3a: n=1
4a: n=2

2b: n=0
3b: n=1
4b: n=2

hν
hν'

5a: n=1
6a: n=2

5b: n=1
6b: n=2

hν
hν'

Scheme 3

hν
△

7a: Ar=
8a: Ar= —Me
9a: Ar=
Me

7b: Ar=
8b: Ar= —Me
9b: Ar=
Me

$CH_2CH_2CH_3$
$H_3CH_2CH_2C$ OH
HO

10a

hν
△

$CH_2CH_2CH_3$
$H_3CH_2CH_2C$ OH
HO

10b

Scheme 4

corresponding biradical **10b** on UV or sunlight irradiation. The photogenerated biradical exhibited antiferromagnetic interactions on account of the singlet ground state and a thermally accessible triple state in this case.[22]
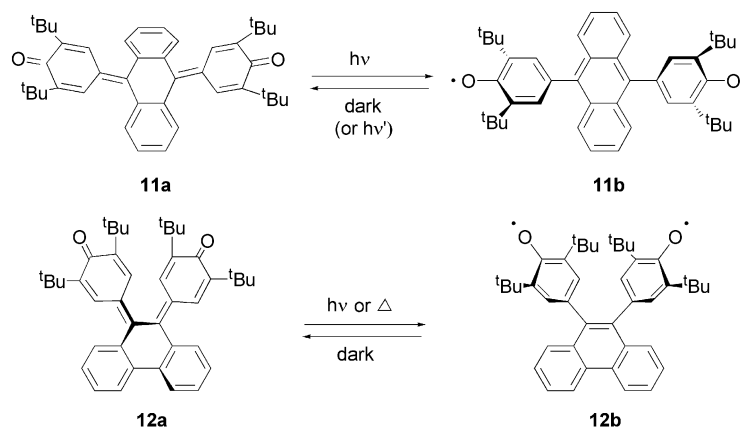
2-4 Organic biradical compounds with terphenoquinone unit

This system is also regarded as type I (B). Dibenzoannulated 3,5,3″,5″-tetra(*tert*-butyl)-*p*-terphenoquinone was prepared by Oda *et al.* and the compound was found to show a reversible, photochemical–thermal isomerization between the quinone and diradical forms, involving restricted conformational change (Scheme 5).[23] EPR signals appeared immediately when a degassed benzene solution of **11a** was irradiated with a 500 W Xenon lamp, indicating the formation of diradical **11b** and the intensity rapidly increased with time, reaching maximum within 5 min. The signals decreased in turn in the dark and thus, in spite of the low concentration of the diradical **11b** (as low as about 4%) and the somewhat slow thermal back process, this system substantiates a molecular switch in principle. A related terphenoquinone, dibenzo-*o*-terphenoquinone derivative **12a**, was successively prepared by the same group more recently and the compound was found to be in
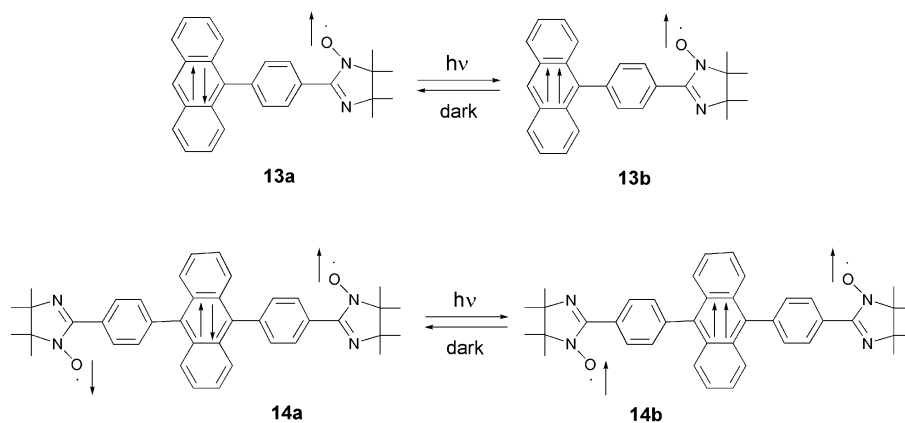
a slight equilibrium with its diradical form **12b**, showing a photo-responsive switching property traceable by EPR spectroscopy.[24] Irradiation of **12a** with a high pressure Hg lamp causes a gradual increase of EPR signal intensity owing to the formation of the corresponding diradical **12b**, which returns to the original intensity in the dark in 1.5 h at room temperature, although the response is slower than the previous one (Scheme 5).

2-5 Organic radical compounds with anthracene unit

The next compounds are type I (C). A 9-phenylanthracene derivative with an iminonitroxide radical at the *para*-position (**13a**) and a 9,10-diphenylanthracene derivative with the radicals at both *para*-positions (**14a**) were designed and synthesized by Teki, Miura *et al.*[25] together with their topological isomers having the radical(s) at *meta*-position(s) (Scheme 6). Time-resolved ESR (TRESR) spectra of the first excited states with resolved fine structure splittings were observed for **13a** and **14a** in an EPA or a 2-MTHF rigid matrix. Using the spectral simulation based on the eigenfield method, the observed TRESR spectra were unambiguously assigned as an excited quartet ($S = 3/2$) spin state (**13b**) or an excited quintet ($S = 2$) spin state (**14b**), respectively, while high-spin excited states were not observed for their topological isomers,

'Bu **'Bu**

11a   hv / dark (or hv')   **11b**

'Bu

12a   hv or △ / dark   **12b**

Scheme 5

13a   hv / dark   **13b**

14a   hv / dark   **14b**

Scheme 6

showing the crucial role of π-topology in the spin alignment of the excited states.

Since a weak antiferromagnetic exchange interaction was observed in the ground state of **14a**, the clear detection of the excited quintet high-spin state shows that the effective exchange coupling between the two radicals through the diphenylanthracene spin coupler has been changed from antiferromagnetic to ferromagnetic upon excitation and thus a photo-induced spin alignment utilizing the excited triplet was realized in the purely organic π-conjugated spin system.

2-6 Organic radical compounds with naphthopyran unit

These are classified as type I (D). A couple of naphthopyran derivatives with stable radical substituents **15a** and **16a** were prepared from the ethynylated alcohol of Michler's ketone and 2,6-dihyroxynaphthalene. Irradiation of **15a** and **16a** with the light of 365 nm in carbon tetrachloride gave gradually reddish precipitates, which were found to be the desired compounds **15b** and **16b**, respectively. It was found that the open-formed species could be changed back to the original naphthopyrans in relatively high yields by the treatment of **15b** and **16b** with a catalytic amount of SiO_2 in acetonitrile at ambient temperature (Scheme 7).[26]

Although antiferromagnetic interactions were observed for both **15a** and **16b**, a distinct difference is discerned for their Curie constants as well as Weiss temperatures. The large decrease of the Curie constant of **15b** suggests the singlet formation between the spin centers in the compound. A similar difference was confirmed between the Curie constants of the couple **16a/16b**, though the signs and the magnitude of their intermagnetic interactions are more largely different in this case than the former couple. Furthermore, the decreased Curie constant of **15b** was found to

NMe_2 Me_2N^+ NMe_2

hv / CCl$_4$ / SiO$_2$

$R-C-O-$ $-O-C-R$

15a : R =   **15b** : R =

16a : R =   **16b** : R =
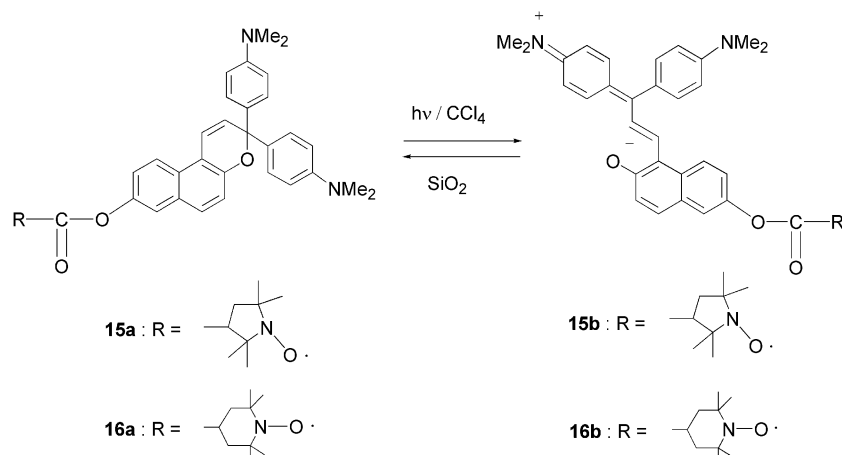
Scheme 7

revive to almost the original value of **15a**. Thus, the apparent tuning of their Curie constants together with their Weiss temperatures was found to be possible in these two reversible couples, in principle, by choosing the outer stimuli of light and a catalyst.

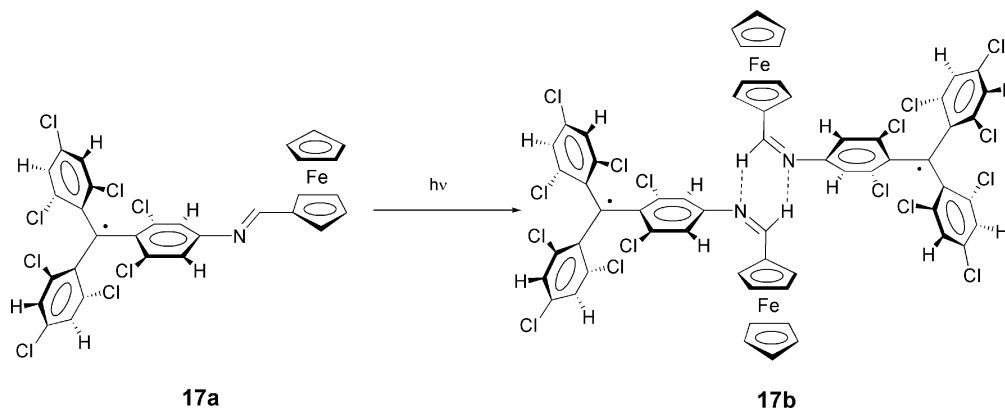# 3 Organic photo-responsive radicals based on intermolecular structural change

Several organic radical compounds with photo-responsive properties that exhibit changes of their magnetic properties upon irradiation and that are based mainly on the *intermolecular structural change* will be introduced and discussed in this section. These include a ferrocenyl Schiff base derivative with tris-(2.4.6-trichlorophenyl)methyl radical as well as hexaarylbiimidazoles.

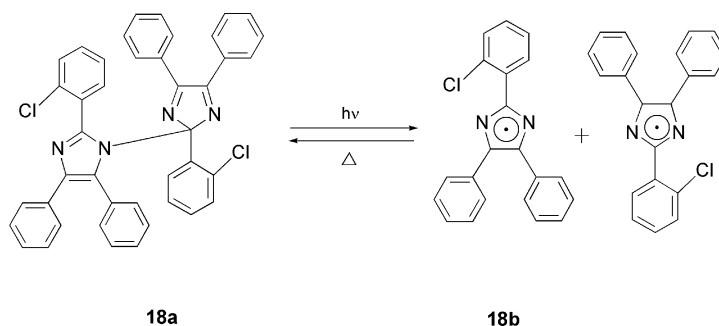## 3-1 Organic radical compound with arylimine units

This example is apparently classified as type II (A). A ferrocenyl Schiff base polychlorotriphenylmethyl radical **17a** was prepared by Veciana *et al*. through a condensation reaction between the (4-amino-2,6-dichlorophenyl)methyl radical and ferrocene mono-carboxaldehyde and was isolated as a mixture of *trans-* and *cis-* isomers, from which each isomer could be successfully separated. The *in situ* irradiation of the *trans*-isomer showed a neat transformation to the *cis*-isomer **17b** with a significant change in the EPR spectra, whereas the reverse photoisomerization process could not be observed, when monitored by EPR and/or Uv/vis spectroscopy (Scheme 8).[27]

Interestingly, the *cis*-isomer aggregates in solution at low temperatures through hydrogen bonding to give thermodynamically stable diradical dimers with strong antiferromagnetic interactions and, thus, represents an interesting example of a photomagnetic system based on a photochemical dimerization due to supramolecular process.

It is noted that a similar intermolecular approach has recently been reported by using anthracene and the corresponding dimer system bearing aminoxyl radicals.[9]

3-2 Organic lophyl radicals from hexaarylbiimidazoles

Those examples are classified as type II (B). It is well known that hexaarylbiimidazole derivatives are readily cleaved by irradiation to give a pair of triaryl radicals called lophyl radicals that can recombine to form the original biimidazoles (lophine dimers).[28] More recently, it was reported that at low temperatures of *ca.* 10 K the ultraviolet irradiation of 2-chlorohexaarylbiimidazole **18a** produces a triplet hexaarylbiimidazole rather than the radicals, but that at higher temperatures formation of the corresponding radicals **18b** from the dissociation of the singlet state dominates (Scheme 9).[29] On the same compound, using irradiation with a high-pressure mercury lamp, the *in situ* direct observation of a light-induced radical pair in a crystal was successfully carried out recently to see for the first time the structural features of the radical pairs below 103 K.[30] The structure and the EPR spectral properties of the light-induced radicals were further investigated by Abe *et al*. to prove the existence of two sorts of triplet radical pairs A and B.[31]

It was found from the EPR investigation on the samples after photolysis at very low temperatures that the triplet state of pair A could be the ground state or is nearly degenerate with the singlet state, while the observed triplet state in pair B is thermally populated and the singlet state is the ground state, enabling the determination of the intermolecular exchange coupling (2*J*) to be -77 cm^{-1} and the pair B was found to be the actual species observed in the X-ray study at 103 K. Moreover, the calculated results by the spin-polarized density functional theory (DFT) agree well with the experimental results to provide an accurate description even for the through-space coupling in the radical pair.

Thus the formation of radical pairs is strictly verified in this class of photochromic processes to envisage the hexaarylbiimidazole and related derivatives[32] as promising candidates for photo-responsive spin systems.

4 Summary and future prospects

In this article, recent studies toward the exploitation of organic spin systems with photo-responsive magnetic properties are briefly surveyed, focusing mainly on the structural variation of the organic

Scheme 8

Scheme 9

radical compounds so far reported. It would be true to say that the organic spin systems described above are still in their infancy from the viewpoint of magnetic switching systems and there still are some limitations in organic photo-responsive systems, *e.g.*, relative instability of organic radicals on exposure to light (and heat), insufficient fatigue durability in general, relatively small magnitude of spin–spin interactions in organic spin systems, less efficient switching of magnetic interactions in general, when compared to some efficient inorganic counterparts including widely studied spin cross over systems.[33] But, nevertheless, the structural versatility of organic radicals and photochromic systems will surely provide a wide range of possible candidates of organic photo-responsive spin systems. Hence this field of chemistry will remain attractive and worth challenging and be further broadened with the structural elaboration of organic systems together with the fabrication of organic–inorganic hybrid systems, although probably changing the tone of its colour in some way. In this context, the molecular, supramolecular, and even crystal design of photo-responsive spin systems will be crucial for constructing eminent photo-responsive spin systems and to realize efficient switching of spin–spin interactions.

References

1 For the recent reviews on photochromism, see for example, Photochromism: Memories and Switches, *Chem. Rev.*, 2000, **100**(5) (Special Issue), ed. by M. Irie.
2 M. Fritsche, *Comp. Rend.*, 1867, **69**, 1035.
3 E. ter Meer, *Ann. Chem.*, 1876, **181**, 1.
4 M. Gomberg, *Ber. Dtsch. Chem. Ges.*, 1900, **33**, 3150.
5 W. Marckwald, *Z. Phys. Chem.*, 1899, **30**, 140.
6 G. Scheibe and F. Feichtmayr, *J. Phys. Chem.*, 1962, **66**, 2449.
7 For the history of organic magnets, see, J. S. Miller, *Adv. Mater.*, 2002, **13**, 1105.
8 S. Nakatsuji and H. Anzai, *J. Mater. Chem.*, 1997, **7**, 2161.
9 S. Nakatsuji, *Adv. Mater.*, 2001, **13**, 1719.
10 . O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science*, 1996, **272**, 704.
11 K. Nagai, T. Iyoda, A. Fujishima and K. Hashimoto, *Solid State Commun.*, 1997, **102**, 809.
12 *Cf.* N. Koga and H. Iwamura, in *Magnetic Properties of Organic Materials*; ed. P. M. Lahti, Marcel Dekker, Inc., New York, Basel, 1999, Chapt. 30, p. 629.
13 K. Hamachi, K. Matsuda, T. Itoh and H. Iwamura, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 2937.
14 A photochromic molecular-based magnet, MnCr(ox)$_3$/H$_2$O complex of a spiropyran derivative; S. Bénard, E. Riviere, P. Yu, K. Nakatani and J. F. Delouis, *Chem. Mater.*, 2001, **13**, 159.
15 Photoinduced magnetization in the organic-based magnet Mn(TCNE)$_x$·(CH$_2$Cl$_2$)$_y$; D. A. Pejakovic, C. Kitamura, J. A. Miller and A. J. Epstein, *Phys. Rev. Lett.*, 2002, **88**, 57202.
16 Magnetic behavior of a 3:2 mixture of Cu(II) (hfacac)$_2$ and 1,3,5-benzenetriyltris(4-pyridyldiazomethane) in a frozen solution after irradiation: photochemical formation of a solid solution magnet; S. Karasawa, H. Kumada, N. Koga and H. Iwamura, *J. Am. Chem. Soc.*, 2001, **123**, 9685 and references therein.
17 K. Matsuda and M. Irie, *J. Am. Chem. Soc.*, 2000, **122**, 7195.
18 K. Matsuda and M. Irie, *J. Am. Chem. Soc.*, 2000, **122**, 8309.
19 K. Matsuda and M. Irie, *Chem. Eur. J.*, 2001, **7**, 3466.
20 K. Matsuda, M. Matsuo and M. Irie, *J. Org. Chem.*, 2001, **66**, 8799.
21 K. Tanaka and F. Toda, *J. Chem. Soc., Perkin Trans. 1*, 2000, 873.
22 L. Xu, T. Sugiyama, H. Huang, Z. Song, J. Meng and T. Matsuura, *J. Chem. Soc., Chem. Commun.*, 2003, 2328.
23 H. Kurata, T. Tanaka and M. Oda, *Chem. Lett.*, 1999, 749.
24 H. Kurata, Y. Takehara, T. Kawase and M. Oda, *Chem. Lett.*, 2003, 538.
25 Y. Teki, S. Miyamoto, M. Nakatsuji and Y. Miura, *J. Am. Chem. Soc.*, 2001, **123**, 294.
26 T. Kaneko, H. Akutsu, J. Yamada and S. Nakatsuji, *Org. Lett.*, 2003, **5**, 2127.
27 I. Ratera, D. Ruiz-Molina, J. Vidal-Gancedo, K. Wurst, N. Daro, J.-F. Lètard, C. Rovira and J. Veciana, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 919.
28 T. Hayashi and K. Maeda, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 429 and their earlier papers.
29 X.-Z. Qin, A. Liu, A. D. Trifunac and V. V. Krongauz, *J. Phys. Chem.*, 1991, **95**, 5822.
30 M. Kawano, T. Sano, J. Abe and Y. Ohashi, *J. Am. Chem. Soc.*, 1999, **121**, 8106.
31 J. Abe, T. Sano, M. Kawano, Y. Ohashi, M. M. Matsushita and T. Iyoda, *Angew. Chem. Int. Ed.*, 2001, **40**, 580.
32 K. Okada, K. Imamura, M. Oda, M. Kozaki, Y. Morimoto, K. Ishino and K. Tasiro, *Chem. Lett.*, 1998, 891.
33 P. Gütlich, A. Hauser and H. Spiering, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2024.