Thermochromism in an organic crystal based on the coexistence of σ- and π-dimers

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Transition-metal complexes and organic radical molecules can be used to make electric conductors and ferromagnets[1–3], the optical properties of which can be controlled by changing temperature and are used as molecular switches and sensors[4–8]. Whereas a number of organic radicals in solution show temperature-dependent optical properties[5,6,9–12], such behaviour in crystalline forms is more rare[13–15]. Here, we show a fully reversible continuous thermochromism with a unique mechanism in purely organic crystals of diazaphenalenyl radical. This behaviour is based on changes in the diazaphenalenyl dimers coexisting in the crystal. From the X-ray crystal structure analyses and temperature-dependent visible spectra, we conclude the presence of a thermal equilibrium between σ-bonded and π-bonded dimers, which are separated by 2.62(6) kcal mol^{-1}. This conclusion is supported by room-temperature electron spin resonance spectra of the solid, which showed signals that are attributable to a thermally accessible triplet state of the π-dimer structure. This proves the coexistence of two dimers of different bonding natures in the crystal, causing it to demonstrate thermometer-like behaviour.

Organic radicals are generally known as unstable and highly reactive species at room temperature under air atmosphere. Chemical modification for the stabilization and isolation of organic radicals, however, enabled significant potential as spin sources for molecule-based magnetic materials[1,2]. A number of organic radicals in solution show changes in their optical properties depending on temperature owing to the existence of the equilibrium between the monomer and the dimer of the radical[5,6,9–12]. Furthermore, it is also well known that crystals of some complexes of cobalt and iron show temperature-dependent optical properties accompanied by valence tautomerism and spin crossover[7]. In contrast, few organic radicals in the crystalline states show those behaviours. As such rare examples, crystals of trithiatriazapentalenyl[13,14] and spiro-biphenalenyl[15] exhibit sudden and simultaneous changes in their magneto-optical properties due to structural phase transitions at specific temperatures.

Phenalenyl derivatives have attracted great attention as model systems to realize spin-mediated molecular functionalities[8,15,16]. It is well illustrated by the tri-*t*-butylated phenalenyl system **1** (Fig. 1a) that the highly symmetrical (D_{3h}) and fully delocalized nature of the electronic spin structure of this system leads this radical to form parallel stacked dimer structures in the solid state, as well as in solution at low temperature[11,12,17]. In contrast, symmetry-breaking incorporation of two nitrogen atoms at positions 1 and 3 of **1** (compound **2**, Fig. 1a) has been found to result in the formation of an angled face-to-face *syn*-dimer structure and a strongly asymmetric bonding nature in the crystal that show large temperature factors and a high anisotropy at 296 K (Fig. 1b)[18]. These features are associated with a colour change between 100 K (colourless or extremely pale green) and 430 K (dark green) (Fig. 2; Supplementary Information, Figs S1,S2), in contrast to crystals of trithiatriazapentalenyl and spiro-biphenalenyl which do not show such thermochromism. Crystals of **2** are extremely stable in atmosphere with no significant decay of the colour for years.

Here, we have carried out X-ray structure analyses of a crystal of **2** at five different temperatures and the results of these analyses help us to understand this thermochromism: they show that the two carbon atoms having large temperature factors and a high anisotropy at 296 K (ref. 18) can be identified as two different kinds of carbon atom (see Supplementary Information, Fig. S3). Apparently, an angled σ-bonded dimer (σ-dimer) and a parallel stacked dimer (π-dimer) coexist and interconvert in the crystal (Fig. 3a,b). The structure of each dimer is independent of temperature variation, whereas the population of the two dimers (otherwise unchanged) in the crystal changes with temperature: the number of σ-dimers decreases on increasing the temperature,

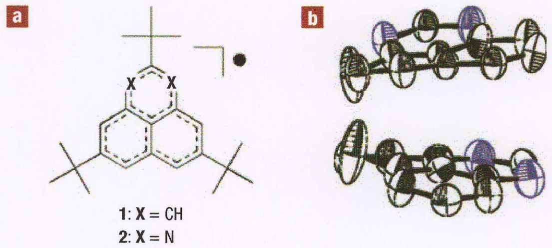

Figure 1 Molecular formula and crystal structure of compound 2. a, Compounds **1** and **2**. **b**, Angled face-to-face *syn*-dimer structure in the crystal at 296 K (ref. 18). The black and blue ellipsoids denote carbon and nitrogen atoms in the diazaphenalenyl skeleton, respectively. The *t*-butyl groups are omitted for clarity. Two of the carbon atoms have large temperature factors and high anisotropy.

Figure 2 Images of the 0.15-mm-thick crystal of 2 in the range of temperature between 100 K and 300 K. These images and the further gradual deepening of the green colour on increasing the temperature from 300 K to the decomposition point at 430 K show a reversible continuous change in colour from colourless (or extremely pale green) to dark green in the wide range of temperature (100–430 K). A monochromatic change of the crystal colour gives a colour thermometer with a high temperature resolution.

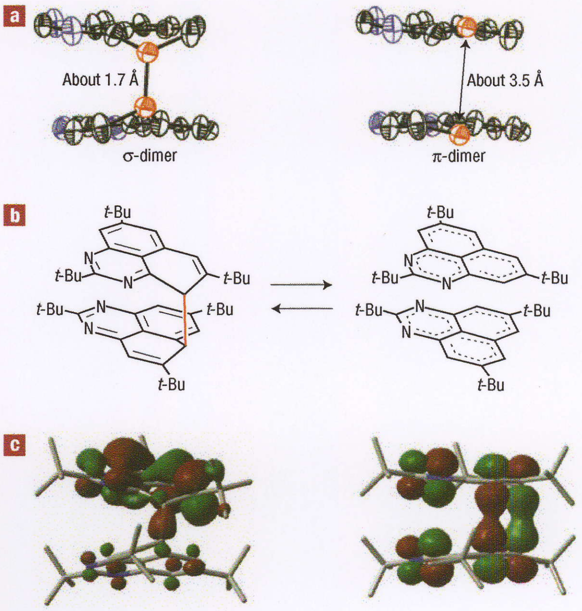

Figure 3 Two types of dimer structure of 2 disordering in the crystalline state. a, Two of the carbon atoms having large temperature factors and high anisotropy can be identified as two kinds of carbon atom under the specific restraint condition of the X-ray analyses (see Supplementary Information, Fig. S3). These pictures were analysed and extracted from the angled face-to-face *syn*-dimer structure measured at 153 K. The red, black and blue ellipsoids denote the disordered carbon atom, the other carbon, and nitrogen atoms in the diazaphenalenyl skeleton, respectively. The *t*-butyl groups are omitted for clarity. **b**, Schematic drawings of the σ- and π-dimer. **c**, Diagrams of the calculated HOMO of the σ- and π-dimers optimized by the B3LYP/6-31G* method.

whereas that of the π-dimers increases (see Supplementary Information, Fig. S4).

In the temperature-dependent visible spectra of **2** using a KBr pellet, a broad absorption band around 670 nm begins to appear above 250 K (see Supplementary Information, Fig. S5a). Polarized electronic spectra on the (010) surface of the crystal at 300 K showed that the band is strongly polarized along the *c* axis (see Supplementary Information, Figs S2,S5b,S6), which is nearly perpendicular to the plane of the diazaphenalenyl skeleton, indicating that the absorption band is associated with the intradimer excitation as is expected for the π-dimer by analogy with the dimer of compound **1** which shows a very similar band peaking at 595 nm (refs 11,12,17). It is also expected that the σ-dimer composed of two quinazoline moieties linked with a σ-bond (Fig. 3b) does not absorb visible light. On increasing the temperature, the intensity of the 670 nm band in the polarized electronic spectra increases continuously (Fig. 4a, inset), indicating that, on a free-energy scale, the π-dimer lies above the σ-dimer in the crystal.

From the above experimental findings, we conclude that the continuous temperature-dependent colour change in the absence of structural phase transitions is due to a thermal equilibrium, between the σ-dimer, which constitutes the lowest energy state, and the π-dimer, which represents a higher-lying thermally accessible state (or isomer) of **2**. In contrast, radical **1** does not show any thermochromism in the crystalline state, which suggests that the symmetry lowering (C_{2v}) of the spin density distribution caused by the two nitrogen atoms plays a pivotal role in the ability of **2** to form a σ-dimer in equilibrium with the π-dimer.

The energy gap between the two dimer states ($\Delta E_{\sigma-\pi}$) was determined by the temperature-dependent changes of the oscillator strength (f) for the π-dimer at 450–850 nm in the polarized electronic spectra (Fig. 4a). On the assumption that the ratio of the π-dimer to all of the dimers obeys the Boltzmann distribution, f is described by the following equation:

$$f = C\frac{\exp(-\Delta E_{\sigma-\pi}/kT)}{1+\exp(-\Delta E_{\sigma-\pi}/kT)},$$

where C is a proportional constant, k is the Boltzmann constant and T is temperature. The energy gap ($\Delta E_{\sigma-\pi}$) thus obtained was $1.32(3) \times 10^3$ K or 2.62(6) kcal mol^{-1} (Fig. 4c). This value is in good agreement with the difference in the total energy of 3.0 kcal mol^{-1} between the optimized π- and the σ-dimer calculated by the B3LYP/6-31G* method (see Supplementary Information, Fig. S7). The energy gap ($\Delta E_{\sigma-\pi}$) in the crystalline

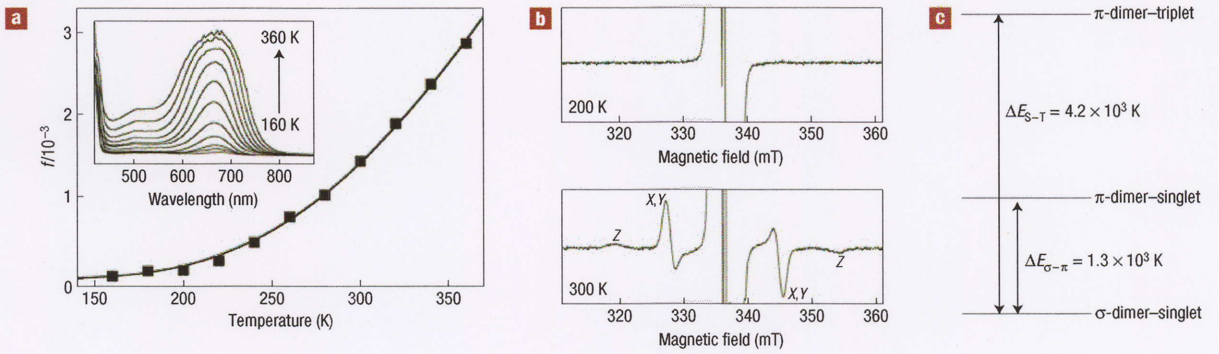

Figure 4 Temperature dependence of the oscillator strength, solid-state ESR spectra and experimentally determined energy diagram of the crystal. a, The oscillator strength for the π-dimer estimated from the polarized electronic spectra (inset) with a 0.13-mm-thick crystal on the parallel direction to the *c* axis at various temperatures (see Supplementary Information, Figs S2,S6). The solid line represents calculated values for $\Delta E_{\sigma-\pi} = 1.32 \times 10^3$ K. **b**, Solid-state ESR spectra observed at 200 K and 300 K. Fine-structure triplet-state ESR signals with axial symmetry are clearly seen in addition to the central intense signal from the monoradical impurities (about 0.1%) arising from lattice defects[18]. The experimental *D* and low *E* values close to those of **1** indicate that the electronic spin structure of the triplet state of **2** is attributed to a thermally accessible excited state with a similar π-dimer structure (see Supplementary Information, Fig. S12). **c**, Experimentally determined energy diagram of **2** of the crystal.

state was significantly smaller than the dissociation enthalpy of the σ-dimer of **2** in solution (12 kcal mol^{-1}) determined from electron spin resonance (ESR) spectra (see Supplementary Information, Figs S8,S9). The difference is attributed to the bonding nature in the π-dimer, which is clearly seen in the pictures of the highest occupied molecular orbitals (HOMOs) of the σ- and π-dimers (Fig. 3c, Supplementary Information, Fig. S10). The bonding between the two diazaphenalenyl moieties in the σ-dimer is only through the σ-bond because there is hardly any overlap of the π-MOs in the HOMO. In contrast, multiple bonding overlap of the π-MOs is seen in the HOMO of the π-dimer, which is similar to the case of the symmetrical π-dimer for radical **1** (refs 11,12,17).

To elucidate the bulk magnetic properties and relevant spin states of **2**, we previously measured the magnetic susceptibility of the polycrystalline solid from 1.8 to 350 K at 0.1 T (see Supplementary Information, Fig. S11)[18], and found that the crystals of **2** exhibit a weak paramagnetism from a small amount of radical impurities (about 0.1%) below 250 K, and slight increase in $\chi_{\mathrm{para}}T$ on increasing the temperature above 250 K (ref. 18). These results suggested that the ground states of σ- and π-dimers are singlets, but that a triplet state may be thermally accessible above 250 K (ref. 18). In the room-temperature ESR spectrum of the polycrystalline sample of **2**, the axially symmetric $\Delta M_S = \pm 1$ transitions of a triplet state were indeed detected (Fig. 4b, lower trace). The spin parameters of this triplet ($S = 1$, $g = 2.004$, $|D|/hc = 0.0173$ cm^{-1} and $|E|/hc < 10^{-3}$ cm^{-1}) closely resemble those for **1** ($S = 1$, $g = 2.003$, $|D|/hc = 0.0167$ cm^{-1} and $|E|/hc < 10^{-3}$ cm^{-1}), which has a π-dimer structure in the crystalline state (see Supplementary Information, Fig. S12)[17,18]. From this we concluded that the triplet state that is detected above 250 K also has a π-dimer structure. Notably, these ESR signals vanish at 200 K (Fig. 4b upper trace), indicating that the triplet state of **2** is attributed to a thermally accessible excited state of the π-dimer structure. The very small *E* value is also in good agreement with the symmetry of the HOMO and the lowest unoccupied molecular orbital for the π-dimer of **2** (see Supplementary Information, Fig. S10).

From the temperature dependence of the triplet-state ESR signal, we determined, using a model that takes into account two singlet states (corresponding to the σ- and π-dimers) and an excited π-dimer triplet state, that the energy gap between σ-dimer–singlet and π-dimer–triplet (ΔE_{S-T}) is $4.19(2) \times 10^3$ K or 8.33(4) kcal mol^{-1}. Therefore, a complete energy diagram of the dimer of **2** in the crystalline state can be described as in Fig. 4c. Note that this is the first example where the energy levels of open-shell organic molecules with three energy states have been experimentally located.

We have thus found that the crystal of **2** behaves as a molecular colour thermometer. The phenomenon is associated with the coexistence of σ- and π-dimer structures in the crystal and the electronic nature of the bonding in these dimers. We have identified a unique molecular system where three energy states of the dimer of a radical coexist in the crystal, that is, a σ-dimer, a π-dimer singlet and a thermally accessible triplet. These unique molecular and electronic/spin structures as well as the colour thermometer functionality are based on the spin-delocalized nature of the stable phenalenyl system, providing keys to new molecule-based materials and devices with properties that are controllable by external stimuli[4,7,8].

METHODS

2,5,8-tri-*t*-butyl-1,3-diazaphenalenyl (**2**) was prepared according to the reported procedure[18]. Temperature-dependent ESR measurements were carried out on a Brucker ESP 300/350 spectrometer equipped with an Oxford ESR910 temperature controller. X-ray crystallographic measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Cu Kα radiation at the Rigaku Corporation. The defined method of disordered arrangements is described in Supplementary Information, Fig. S3. Temperature-dependent electronic spectra using a KBr pellet were recorded at the Graduate School of Science, Kyushu University. Temperature-dependent polarized electronic spectra using the single crystal of **2** were taken by using a specially designed spectrometer at the Graduate School of Frontier Sciences, University of Tokyo.

The oscillator strength of the π-dimer is obtained from the polarized electronic spectra by the following equation: $f = 4cm\varepsilon_0/Nhe \times \int \alpha \mathrm{d}(\mathrm{PE})$, where c is the speed of light, m is the electron mass, ε_0 is the electric constant, N is number of σ- and π-dimers per volume unit (m^3), h is Planck's constant, e is the electron charge and $\int \alpha \mathrm{d}(\mathrm{PE})$ is the integral value of the absorption coefficient (α) of the crystal between 1.458 eV and 2.754 eV of photon energy (PE, 850 nm to 450 nm of wavelength). Temperature (T) can be estimated in a reproducible manner by using the following equation with $\Delta E_{\sigma-\pi}$ of 1,320 K and oscillator strength 'f' of the crystal: $T/\mathrm{K} = 1{,}320 \times \ln(f/0.118\text{–}1)^{-1}$.

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Author contributions

Y.M., S.S., K.F., T.T. and K.N. planned this project, and carried out the experimental and theoretical work with the other authors. A.N., S.N., D.S. and K.S. carried out the ESR and magnetic susceptibility measurements and analyses. H.K. (Kyushu Univ.), H.K. (Univ. of Tokyo) and H.O. measured the temperature-dependent electronic spectra. A.S., Y.O., M.S. and K.S. (Rigaku Corp.) carried out the X-ray crystal structure analysis.