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## COMMUNICATION

## Photochemical control of a highly efficient addition reaction between electron-rich alkynes and tetracyanoethylene<sup>†</sup>

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The electron density of an alkyne moiety is enhanced by the photochromic ring closure of a diarylethene derivative, which allows the thermal addition reaction with a small  $\pi$ -acceptor, tetracyanoethylene, at room temperature.

Cycloaddition–retro-electrocyclizations between electron-rich alkynes and the electron-deficient olefin of tetracyanoethylene (TCNE), which were first reported by Bruce *et al.* for metal–acetylide complexes,<sup>1</sup> attract increasing attention due to the highly efficient addition reaction and the excellent nonlinear optical (NLO) properties of the donor–acceptor (D–A) type products.<sup>2</sup> Previous studies revealed that the high electron density of the alkyne moieties is the key to the efficient reaction under mild conditions. For example, the reaction rapidly proceeds in quantitative yields when strong donors, such as N,N-dimethylanilino (DMA) groups, are employed.<sup>3</sup> Taking into account non usage of metal catalysts, such reactions are regarded as the new-generation 'click chemistry' reactions.<sup>4</sup>

Diederich *et al.* recently achieved further advancement of the reactivity control, *i.e.*, switching the reactivity by the protonation of a DMA group.<sup>5</sup> The neutral DMA donor is capable of activating the alkyne moieties for TCNE addition, whereas the electron-donating power of the protonated DMA moiety decreases significantly. This reactivity change was reasonably explained by the Hammett constants of the substituents. As demonstrated by this example, a reaction control by external stimuli is a powerful method for achieving unusual D–A molecules. One of the most often employed external stimuli is light. Thus, many photochromic molecules have been developed,<sup>6</sup> and it is known that diarylethene derivatives

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undergo reversible isomerisation between open- and closedring isomers upon irradiation with ultraviolet (UV) and visible light and their electronic structure changes can be applied to switching functions in molecular devices.<sup>7</sup> Herein, we report the first successful control of the alkyne reactivity towards TCNE addition by the isomerisation of a photochromic diarylethene derivative (Scheme 1). After TCNE addition, the closed-ring isomer of the diarylethene spontaneously underwent the thermal ring-opening reaction to yield a photochromic molecule with a segregated D–A system.

Diarylethene 1 (Scheme 1) asymmetrically substituted with DMA and phenylethynyl groups was prepared by the sequential substitution reactions with octafluorocyclopentene (Scheme S1, ESI†). The chemical structure of 1 was confirmed by NMR, MS and the X-ray crystal structure analysis‡ (Fig. S1 and Table S1, ESI†). This molecule displayed reversible photochromism in solutions. Upon irradiation with UV light ( $\lambda = 322$  nm), a transparent solution of 1 in hexane turned blue due to the formation of the closed-ring isomer 2 (Scheme 1). The absorption spectrum of the blue solution has a maximum ( $\lambda_{max}$ ) at 618 nm (Fig. S2, ESI†). The conversion ratio from 1 to 2 at the photostationary state under irradiation with 322 nm light was 97%. The subsequent irradiation with visible light ( $\lambda > 520$  nm) returned the blue solution to the colourless one, suggestive of the good reversibility.

Computational calculations on the two isomers, 1 and 2, using the density functional theory (DFT) were performed to get insight into the molecular orbitals and reactivity.



Scheme 1 Controlled TCNE addition to an alkyne moiety of a photochromic diarylethene derivative.

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<sup>†</sup> Electronic supplementary information (ESI) available: Synthesis, X-ray crystal structure analysis, absorption spectra, cyclic voltammograms, thermogravimetric analysis and computational calculation details. CCDC 824641. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc13476k



Fig. 1 HOMOs and LUMOs of (a) 1 and (b) 2 calculated by B3LYP/6-31G\*.

The HOMOs and LUMOs resulting from the calculations are depicted in Fig. 1. For 1, the density in the HOMO is localized on the DMA and the adjacent thiophene ring, and the density in the LUMO on the remote phenyl ring. In contrast, both the HOMO and LUMO of 2 are delocalized over the molecule, which ensures the high electron density on the alkyne moiety. Thus, it is thought that the alkyne of 2 has higher reactivity than that of 1. This result was supported by the <sup>13</sup>C NMR spectra. The alkyne peaks of 1 were detected at 81.63 and 93.76 ppm, while 2 displayed the downfield shift of these peaks to 83.98 and 101.78 ppm, respectively.

When TCNE was added to a solution of 1 in 1,2-dichloroethane, no reaction occurred at room temperature (Scheme 1). Note that 2-thienylacetylene derivatives required harsh conditions, e.g., 150 °C and 8 h, to undergo TCNE addition.<sup>3b,8</sup> In contrast, the absorption spectrum of 2 in 1,2-dichloroethane displayed a gradual change upon TCNE addition at room temperature (Fig. 2). The  $\lambda_{max}$  peak of **2** at 643 nm started to decrease, while a new lower-energy band appeared at 987 nm, suggesting the formation of D-A conjugated closed-ring diarylethene 3. This near-infrared band is ascribed to the intramolecular charge-transfer (CT) from donor to acceptor moieties through the diarylethene spacer, as suggested by timedependent (TD) DFT calculations (Fig. S3 and S4, ESI†).9 However, the intensity increase was immediately saturated in 10 min, and the subsequent decrease of the CT band implied the thermal ring opening to yield 4. Similar thermal ring-opening reactions were previously reported for other diarylethene derivatives substituted by both donor and acceptor groups.<sup>10</sup>



**Fig. 2** Time-dependent absorption spectral changes of (a) **2** in 1,2-dichloroethane at 20  $^{\circ}$ C after the addition of a stoichiometric amount of TCNE ((b) 0 min, (c) 10 min, (d) 20 min, (e) 30 min, (f) 40 min, (g) 50 min, (h) 60 min, (i) 90 min).

This spontaneous transformation completed in 90 min, and the isolated yield of **4** by HPLC amounted to 95%. The chemical structure of **4** was unambiguously characterized by <sup>1</sup>H and <sup>13</sup>C NMR, FT-IR spectroscopies and mass spectrometry (ESI<sup>†</sup>). **4** is a D–A substituted photochromic molecule which changes its optical absorption in the near-infrared region. UV light irradiation to a solution of **4** in 1,2-dichloroethane gave rise to the near-infrared absorption band, suggesting the light-induced ring-closure reaction to **3** (Fig. S5, ESI<sup>†</sup>).

The continuous reaction progress from 2 to 4 was also monitored by cyclic voltammograms (CVs) in acetonitrile at room temperature. The mixture of 2 and TCNE displayed a DMA-centred reversible one-electron oxidation at 0.07 V (vs. ferrocene/ferrocene<sup>+</sup> ( $Fc/Fc^{+}$ )) and an irreversible reduction peak ascribed to TCNE at -0.47 V (Fig. S6, ESI<sup>†</sup>). This CV slowly changed as a set of the reactions proceeded. For example, the original peaks became equivocal, and an anodically-shifted new oxidation and cathodically-shifted new reduction peaks appeared after 20 and 30 min, respectively. These new peaks became sharp as time went on, and the original peaks almost completely disappeared after 60 min, which was consistent with the absorption spectral change. However, other sharp oxidation and reduction peaks were also detected at -0.24 and -0.47 V, respectively, which were probably ascribed to the redox of a side product caused by the repeated potential sweeps.

In order to assign the detected redox potentials, CVs of 1, 2 and 4 were measured and the redox potentials are summarized in Table 1. Although 1 showed only the first oxidation potential  $(E_{\text{ox},1})$ , 2 displayed both the  $E_{\text{ox},1}$  and the first reduction potential  $(E_{\text{red},1})$  in the measurement range (Fig. S7, ESI<sup>†</sup>). On the other hand, 4 exhibited an anodically-shifted, DMA-centred  $E_{\text{ox},1}$  at 0.33 V as well as two reduction potentials ( $E_{\text{red},1}$  and  $E_{\text{red},2}$ ) ascribed to the 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) moiety at -0.62 and -0.96 V. These potentials were consistent with the new peaks emerging in the *in situ* CVs. The electrochemical band gap (0.95 V) of 4, calculated from  $E_{\text{ox},1}$  and  $E_{\text{red},1}$ , was close to the optical band gap determined from the end absorption ( $\lambda_{\text{end}} = 1320$  nm: 0.94 eV) of 3 (Fig. S5, ESI<sup>†</sup>).

It is also known that 7,7,8,8-tetracyanoquinodimethane (TCNQ), which is an expanded analogue of TCNE, undergoes the addition reaction to the electron-rich alkynes by a similar mechanism.<sup>11</sup> However, TCNQ did not react with **2** under the same conditions. Heating to 70 °C resulted in the thermal ring opening from **2** to **1** without the occurrence of the addition reaction.

Absorption spectra of 1 and 4 were measured in various organic solvents, and the data are summarized as a function of solvent polarity  $E_{\rm T}$  (30) (Fig. S8 and Table S2, ESI<sup>†</sup>). Both compounds displayed positive solvatochromism and the extent

**Table 1** Summary of electrochemical data of 1, 2 and  $4^a$ 

	$E_{\rm red,2}/{\rm V}$	$E_{\rm red,1}/{ m V}$	$E_{\rm ox,1}/{\rm V}$
1 2 4	 	$-1.57^b$ -0.62	$0.17 \\ 0.06^{b} \\ 0.33$

<sup>*a*</sup> Measured in acetonitrile with 0.1 M tetra-*n*-butylammonium perchlorate at 20 °C. Potentials *vs.* Fc/Fc<sup>+</sup>. <sup>*b*</sup> Peak top potentials.

of this feature was more significant for **4** than for **1**, suggestive of the larger dipole moment.

Durability of diarylethene derivatives against thermal decomposition has not been thoroughly investigated. Thus, the effect of TCNE addition on the thermal durability was also examined. The open-ring diarylethene 1 showed a 5 wt% decomposition temperature ( $T_{d5\%}$ ) of 109 °C under nitrogen flow, whereas that of the closed-ring 2 significantly increased to 272 °C (Fig. S9 and Table S3, ESI<sup>+</sup>). The residual soot amount of 2 at 500 °C was definitely greater than that of 1. Noticeably, the TCNE-adduct 4 still retained the high thermal stability with a  $T_{d5\%}$  of 193 °C, despite the open-ring form of the diarylethene. Furthermore, the soot amount of 4 at 500 °C was similar to that of 2, implying the efficient occurrence of thermally-induced rearrangements of triple bond moieties. Thermal improvements in terms of cyano-based acceptor addition are often observed in the case of the postfunctionalization of polymers.<sup>12</sup>

In conclusion, we have succeeded in controlling the alkyne– TCNE addition reaction by using the isomerisation of the photochromic diarylethene derivative. The facilitated thermal ring-opening of the TCNE-adducted diarylethene allowed the construction of strong acceptor moieties under mild conditions<sup>13</sup> and the production of the D–A substituted photochromic molecule. Also, the combination of plural external stimuli, such as light, pH, and solvent polarity, to realize molecular logic systems will be worthwhile for future work.

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‡ Crystal data of 1:  $C_{31}H_{23}F_6NS_2$ , T = 123(2) K, triclinic,  $P_1^{\overline{1}}$ , a = 11.2172(10) Å, b = 14.1305(12) Å, c = 18.2407(16) Å,  $\alpha = 73.8990(10)^\circ$ ,  $\beta = 82.837(2)^\circ$ ,  $\gamma = 77.2150(10)^\circ$ , V = 2702.8(4) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.444$  g cm<sup>-3</sup>,  $R_1$  ( $I > 2\sigma(I)$ ) = 0.0520, w $R_2$  ( $I > 2\sigma(I)$ ) = 0.1371, CCDC 824641.

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