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Dynamic Diels–Alder Reactions of 9,10-Dimethylanthracene: Reversible Adduct Formation, Dynamic Exchange Processes and Thermal Fluorescence Modulation

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Dedicated to Professor Alain Krief

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Studies of the Diels–Alder reactions between 9,10-dimethylanthracene and cyano-functionalized dienophiles led to the identification and characterization of new dynamic systems under ambient conditions. Among these dienophiles were tricyanoethynylethylene derivatives, which gave access to reversible thermal switching of fluorescent properties through binding to and release of the dimethylanthracene partner.

Introduction

Dynamic covalent chemistry (DCC), initially developed as dynamic combinatorial chemistry, represents the covalent domain[1–3] of chemical systems presenting constitutional dynamics[3] on both the molecular and supramolecular levels. It is based on the implementation of reversible chemical reactions that allow the connection and disconnection of components within a molecular architecture. Processes involving in particular imines and disulfides have been shown to present suitable features (for reviews see ref.[1–3]).

To broaden the scope of DCC, further reactions need to be explored. The Diels–Alder (DA) reaction is particularly attractive in view of, namely, its special electronic features and its synthetic utility and the fact that all atoms present in the starting materials are also present in the adduct (self-contained process).[4] We have shown earlier that DA reactions between fulvenes and cyanoethylenes are reversible at room temperature and fit the basic requirements of DCC. We now describe our studies of reversible DA reactions between 9,10-dimethylanthracene (**1**), playing the role of diene, and cyanoethylenes as dienophiles.

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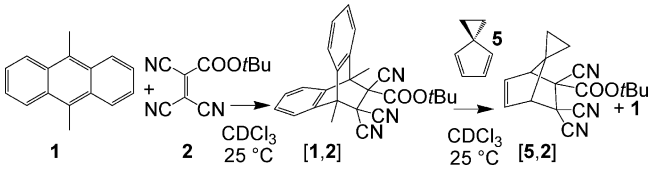
Anthracene derivatives are well-known to undergo DA addition at the 9- and 10-positions (i.e., on its central ring) with a variety of dienophiles.[5] The retro-reaction is possible as well, usually at elevated temperatures. It was first reported that maleimide and various substituted anthracenes were in equilibrium with their adducts in refluxing xylene and that the nature of the substituents at the 9- and 10-positions affected the level of completion of the equilibrium.[6] This reversibility was recently used for transferring the chirality borne by the substituent in the 9-position to the dienophile through the formation of the Diels–Alder adduct, its transformation enantioselectively controlled by the chiral centre next to the bridgehead of the adduct, and finally the retro-Diels–Alder reaction.[7] Supramolecular control of reversible DA reactions on anthracene units contained in a cyclophane has been reported recently.[8] Among the dienophiles that have been used, fullerene plays a particular role owing to its nature and to the low temperature at which its retro-reaction takes place. 9,10-Dimethylanthracene reacts with fullerene at room temperature up to six times, and the adducts formed dissociated reversibly at this temperature.[9]

The development of new covalent systems displaying dynamic properties at room temperature aims at unlocking the potential of DCC. We have previously reported the dynamic Diels–Alder reaction of fulvenes with two specific types of cyanoolefins: the dicyanofumarates and tricyanoethylenecarboxylates.[4] In the present report we describe the reactivity of anthracene derivatives **1** and **6**–**10** with activated dienophiles **2**–**4**, as well as with tricyanoethylene derivatives **11**–**15**.

Results and Discussion

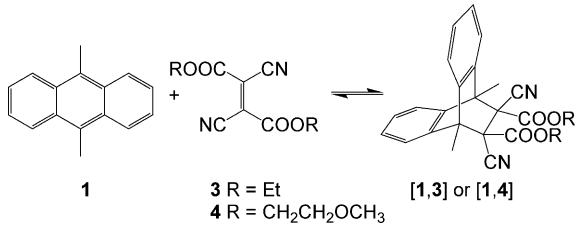
Dynamic Diels–Alder Reactions with 9,10-Dimethylanthracene

In contrast to the case of fulvenes,[4] we observed two different kinetic behaviours for the reactions of 9,10-dimethylanthracene (**1**) with the cyanoolefins mentioned above. The more electron deficient *tert*-butyl tricyanoethylenecarboxylate (**2**) reacted with **1** within 5 min to form quantitatively adduct [**1**,**2**]. For an equimolar 100 mM solution of both reactants in $CDCl_3$, no trace amounts of the starting material were observed by ^1H NMR spectroscopy after 5 min, either at room temperature or after heating to 50 °C. The addition of a diene reacting irreversibly under these conditions with **2**, like spiro[2.4]hepta-4,6-diene (**5**), scavenged the dienophile from [**1**,**2**] and led to the complete liberation of the free anthracene at room temperature, thus demonstrating the reversibility of the reaction of **1** with **2**. The reaction was complete after about 2 weeks with a half reaction time $t_{1/2} < 20$ h (Scheme 1).



Scheme 1. Quantitative reaction of **1** and **2** and subsequent liberation of anthracene after addition of dienophile scavenger **5**.

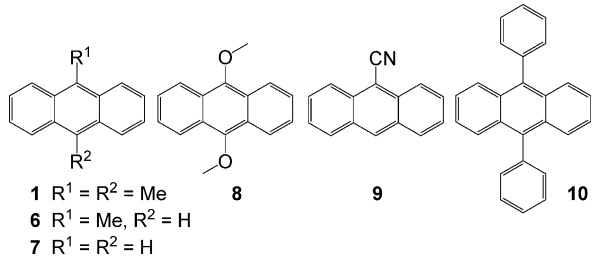
Under the same conditions of concentration and temperature, the reaction of diethyl dicyanofumarate (**3**) with **1** proceeded smoothly and reached an equilibrium within 3 h at room temperature; 98% of the starting material were converted into adduct. The half reaction time was $t_{1/2}$ = 2.5 min. Elevation of the temperature to 50 °C shifted the equilibrium towards the starting materials, reducing the fraction of adduct to 95% (see Scheme 2 and Supporting Information). The same results were observed for bis(2-methoxyethyl) dicyanofumarate (**4**).



Scheme 2. Diels–Alder equilibrium between **1** and **3** or **4** and their adduct [**1**,**3**] or [**1**,**4**].

From these measurements, the association constant of the equilibrium between **1** and **3** and [**1**,**3**] was determined to be 2.4×10^4 M^{-1} at 25 °C and 3.8×10^3 M^{-1} at 50 °C. From these two values, the reaction enthalpy and entropy were calculated to be $\Delta H_{[1,3]} = -60$ kJ mol^{-1} (–13.6 kcal mol^{-1}) and $\Delta S_{[1,3]} = -116$ J mol^{-1} K^{-1} (–26.5 cal mol^{-1} K^{-1}).[10]

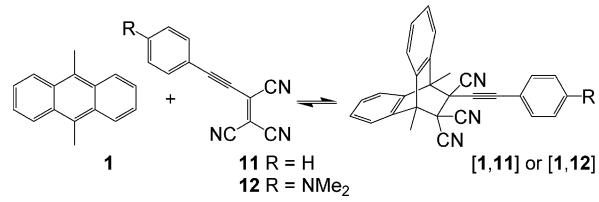
Under the same conditions, the reactions of **3** with 9-methylanthracene (**6**) or anthracene (**7**) led to equilibrium after 30 h and over a week, respectively. In contrast, electron-rich 9,10-dimethoxyanthracene (**8**) did not react with **2** or **3** at room temperature.[11] Instead, the reaction mixture turned brightly coloured, indicating the formation of a charge-transfer complex. In contrast to the reactions of **1** with **2** or **3**, the colour did not disappear with time, as the Diels–Alder reaction did not occur. The same phenomenon was observed when anthracene **9**, bearing an electron-withdrawing cyano substituent in the 9-position was used (see Supporting Information). 9,10-Diphenylanthracene (**10**) did not react with any of the cyanoolefins, and the high steric crowding of the potential adduct might play a role in this lack of reactivity (Scheme 3).



Scheme 3. Structures of the anthracenes tested.

In our efforts to find new dynamic systems based on the Diels–Alder reaction, we then came to consider another family of cyanoolefins. Tricyanoethynylethylenes were first reported in 1990.[12a] In 1995, some more compounds presenting this structure were described, including the first internal charge-transfer compounds in this family.[12b] This scaffold has subsequently been reinvestigated for electrochemical and third-order nonlinear optical properties.[13] In this category of compounds, the strongly electrodeficient 1,1,2-tricyanoethylene moiety, which resembles the tricyanoethylenecarboxylate functionality, is a potential dienophile. In addition, the triple bond affords electronic conjugation of this group with the rest of the molecule, giving access to charge-transfer compounds. Upon Diels–Alder reaction, disconnection of the π conjugation of the three cyano groups occurs, and the electrodeficient moiety can no longer play its electron acceptor role. This feature should permit optoelectronic switching through the Diels–Alder reaction. We therefore investigated the possibility of using these olefins in dynamic covalent chemistry.

We found that 4-phenylbut-1-en-3-yne-1,1,2-tricarbonitrile (**11**) reacted cleanly with **1** at room temperature to form an equilibrium with the corresponding Diels–Alder adduct [**1**,**11**]. This was the first time that a Diels–Alder addition was observed on the C=C bond of a tricyanoethynylethylene. The ^{13}C NMR spectrum of the equilibrated mixture clearly indicated the integrity of the triple bond in the adduct (see Supporting Information). In a mixture with an initial 100 mM concentration in both starting materials in $CDCl_3$, ^1H NMR spectroscopy showed the formation of 95.5% adduct at 25 °C, and this fraction fell to 86% at 50 °C (Scheme 4).



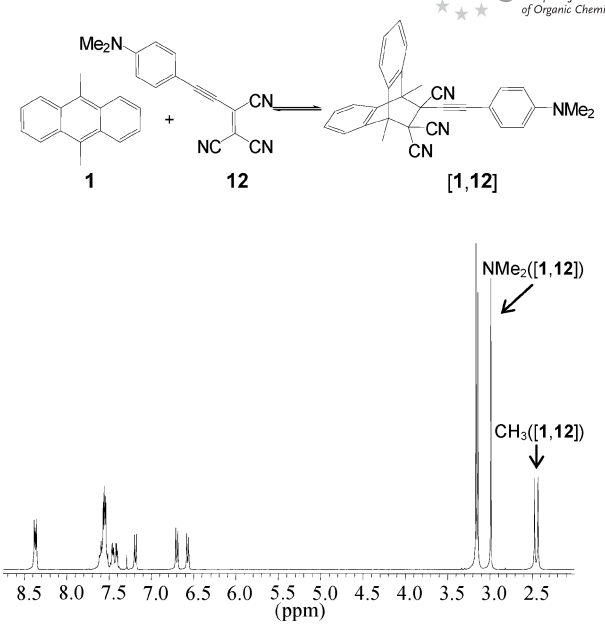
Scheme 4. Diels–Alder equilibrium between **1** and **11** or **12** and their adduct [**1**,**11**] or [**1**,**12**].

From these measurements, the association constants of the equilibrium between **1** and **11** and [**1**,**11**] were determined to be 4720 M^{-1} at 25 °C and 445 M^{-1} at 50 °C. From these two values, the reaction enthalpy and entropy were evaluated to be $\Delta_r H_{[1,11]} = -76$ kJ mol^{-1} (–18 kcal mol^{-1}) and $\Delta_r S_{[1,11]} = -183$ J mol^{-1} K^{-1} (–43 cal mol^{-1} K^{-1}).[10] The kinetics of this system were faster than for **1** and **4**, as the equilibrium is reached in about 60 min at 25 °C with $t_{1/2} <$ 1 min, $k > 0.92$ L mol^{-1} s^{-1} (see Supporting Information).

The same type of dynamic system was formed between **1** and 2-cyano-3-{[4-(dimethylamino)phenyl]ethynyl}but-2-enedinitrile (**12**). In this case, an equilibrium was reached in 10 h, with a half reaction time of $t_{1/2} = 80$ min at 25 °C, where 50% of the starting material was converted into adduct (see Scheme 5 and Supporting Information). At 50 °C, the equilibrium was reached in 50 min, with $t_{1/2} = 10$ min, characterized by the formation of only 24.5% of adduct. The equilibrium constant is therefore 20 M^{-1} at 25 °C and 4.4 M^{-1} at 50 °C. From these two values, the enthalpy and entropy of the reaction were evaluated to be $\Delta_r H_{[1,12]} = -48$ kJ mol^{-1} (–11 kcal mol^{-1}) and $\Delta_r S_{[1,12]} = -138$ J mol^{-1} K^{-1} (–33 cal mol^{-1} K^{-1}).[10] Owing to the slower reaction rates, the rate constants could be determined more accurately and were measured to be $k_{25\,°C} = 1.2 \times 10^{-3}$ L mol^{-1} s^{-1} at 25 °C and $k_{50\,°C} = 2.5 \times 10^{-3}$ L mol^{-1} s^{-1} at 50 °C (see Supporting Information). An enthalpy of activation $\Delta H^{\neq} = 23$ kJ mol^{-1} was derived from these two values.[10]

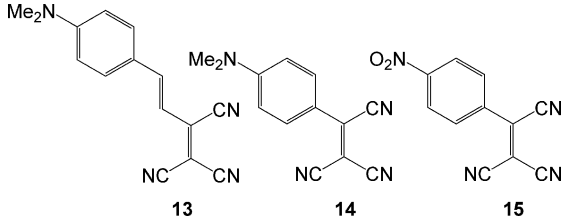
It is interesting to consider the effect of the charge-transfer interaction on the position of the equilibrium. Thus, **11** and **12** differ only by the presence of the *N*,*N*-dimethylamino group, which makes the latter an internal charge-transfer compound and increases the electron density on the dienophile part of the molecule. This effect renders **12** a less-effective component in the Diels–Alder reaction, as illustrated by the difference in the equilibrium constants.

We have also studied the reactivity of (*E*)-4-[4-(dimethylamino)phenyl]buta-1,3-diene-1,1,2-tricarbonitrile (**13**), whose structure is analogous to that of **12**, but where the C≡C bond is replaced by a C=C bond (see Scheme 6). This compound displayed no reactivity towards **1**, neither at 25 °C nor at 50 °C. This result was interpreted as a higher efficiency of the electron transfer between the donor and acceptor groups through the double bond relative to that through the triple bond in **12**, which is a known feature. The 1,1,2-tricyanoethylene group in **13** is thus even less electron deficient than that in **12** and is not reactive as a dienophile. This tendency is also reflected by the chemical shifts of the carbon bearing two cyano groups in the ^{13}C NMR



Scheme 5. Equilibrium between **1** and **12** and their adduct [**1**,**12**] at 25 °C and the corresponding ^{1}H NMR spectrum.

spectra of **11**, **12** and **13**, which is a measure of the electron density of the carbon atom. It was indeed found to decrease along the sequence from 100.5 (**11**) through 91.5 (**12**) to 79.5 ppm (**13**, Table 1). Compounds **14** and **15** bearing a 1,1,2-tricyanoethylene moiety directly on a phenyl group did not react with **1**, neither at room temperature nor at 50 °C. In view of the high electron deficiency expected for the dienophile-like part of **15**, this lack of reactivity might be of steric origin.



Scheme 6. Other molecules containing the 1,1,2-tricyanoethylene moiety tested.

Table 1. Selection of physical data for compounds **11**–**15**.

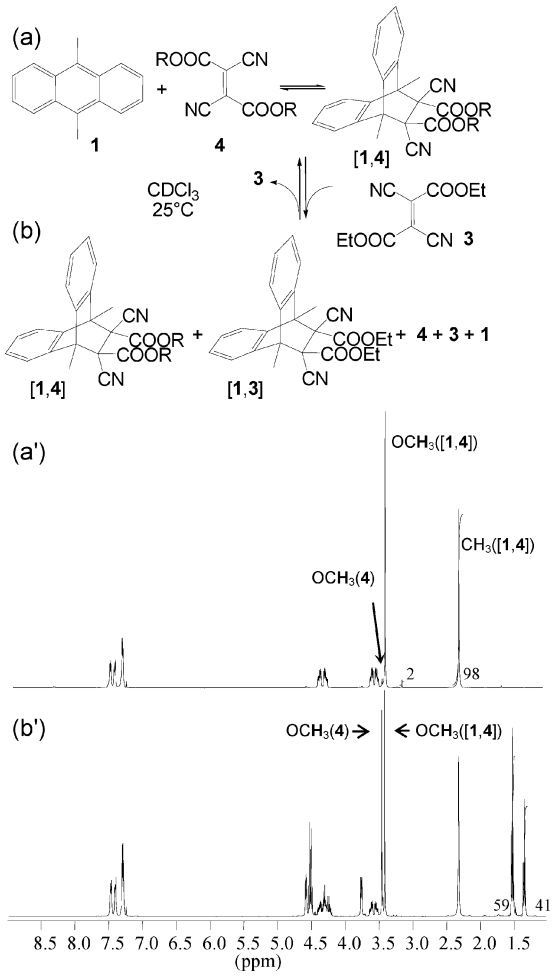
Compound	δ_C{=*C*(CN)$_2$} (ppm)	λ_{max} (nm)
11	100.5	401[a]
12	91.5	591[a]
13	79.5	585[a]
14	77.8	514[b]
15	97.0	

[a] In $CHCl_3$. [b] In acetone.[14]

Component Exchange in the Dynamic Diels–Alder Reactions of 9,10-Dimethylanthracene

We then further explored the dynamic character of these systems by performing competition experiments with the

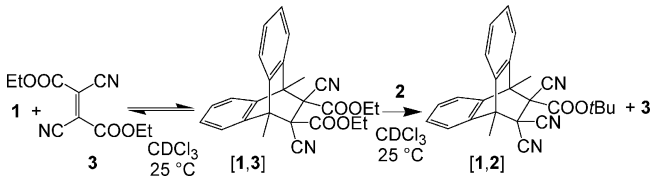
use of two different dicyanofumarates. Bis(methoxyethyl) dicyanofumarate (**4**) reacted with **1** in a similar manner to **3**, leading, at 25 °C, to an equilibrated mixture of **1**, **4** and their adduct [**1**,**4**] (Scheme 7).



Scheme 7. (a) Equilibrium between **1** and **4** and their adduct [**1**,**4**]; (b) competition equilibrium mixture formed after the addition of **3** (1.2 equiv.) to (a); (a′) ^{1}H NMR spectrum of equilibrium (a) in $CDCl_3$ at an initial concentration of 100 mM at 25 °C; (b′) ^{1}H NMR spectrum of the equilibrium mixture (b) obtained after the addition of **3** (1.2 equiv.) to (a). R = $-CH_2CH_2OCH_3$.

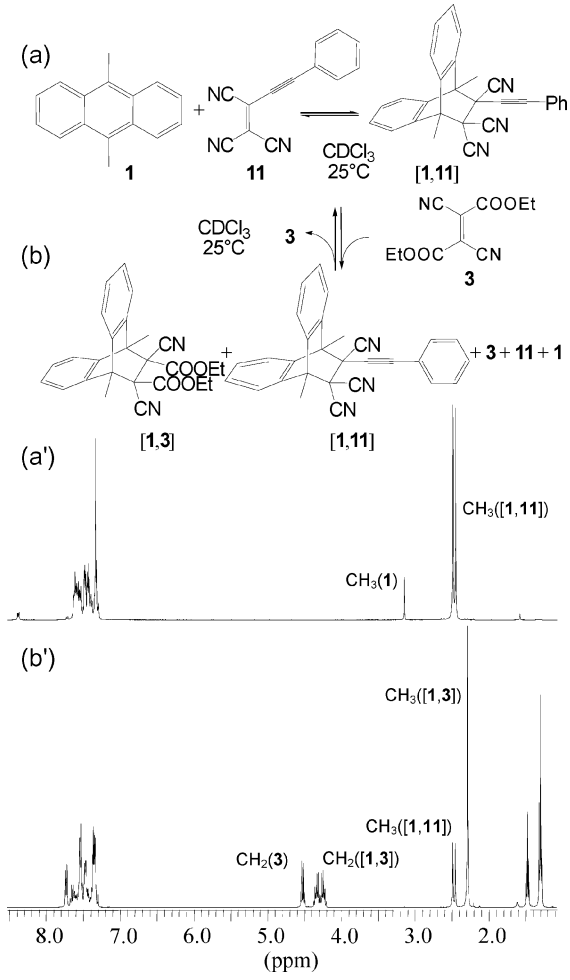
The addition of **3** (1.2 equiv.) led to the appearance of the adduct [**1**,**3**] in a proportion superior to the amount of free anthracene present in the previous equilibrium. The observed competition between the two dienophiles to form a Diels–Alder adduct with **1** demonstrates the dynamic character of the system. The new equilibrium was reached within one week, with a half reaction time $t_{1/2}$ of the order of 16 h, showing an unbiased partitioning between the two adducts [**1**,**3**] and [**1**,**4**], with fractions of free **3** (59.3%) and bound **3** (40.7%) corresponding to the amount of **3** (1.2 equiv.) introduced. The equilibrated mixture is a small dynamic combinatorial library.

A competition between the two different kinds of cyanoolefins was carried out as well, leading to another result. Again, the dissolution of an equal amount of **1** and **3** resulted in the formation of an equilibrated mixture of these starting materials and their adduct. Addition of one equivalent of *tert*-butyl tricyanoethylenecarboxylate (**2**) led to the liberation of the dicyanofumarate in solution. Complete dissociation took as long as 40 d, with a half reaction time of about 1.5 d, leaving no trace of the initial adduct [**1**,**3**]. This result is in line with the higher affinity of tricyanoethylenecarboxylate for the anthracene, with an equilibrium constant at least 10^4 times higher than that for dicyanofumarate,[15] and therefore greater than 10^8 (Scheme 8).



Scheme 8. Total displacement of **3** out of its equilibrium with **1** by the addition of **2** (1 equiv.).

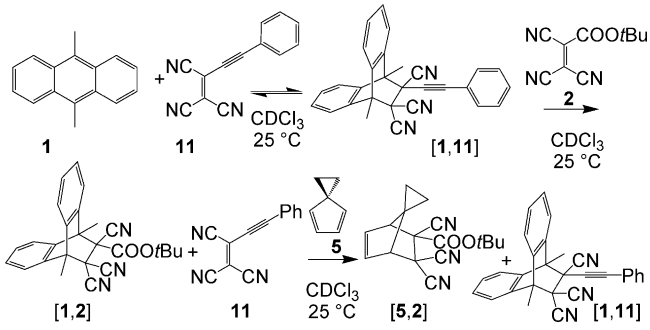
Competition experiments were also carried out with the use of the tricyanoethynylethylenes to further prove the dy-



Scheme 9. (a) Equilibrium between **1** and **11** and their adduct [**1**,**11**]; (b) competition equilibrium mixture formed after the addition of **3** (1.0 equiv.) to (a); (a′) ^{1}H NMR spectrum of equilibrium (a) in $CDCl_3$ at an initial concentration of 100 mM at 25 °C; (b′) ^{1}H NMR spectrum of the equilibrium mixture (b) obtained after the addition of **3** (1.0 equiv.) to (a).

namic character of the system. When diethyl dicyanofumarate (**3**, 1 equiv.) was added to an equilibrated mixture of **1**, **11** and [**1**,**11**], distribution of diene **1** between the two dienophiles **3** and **11** occurred. The new equilibrium was reached within 5 d with a half reaction time $t_{1/2}$ = 10 h. In line with the equilibrium constants, compound **3** displayed a higher affinity for **1** than **11**, as indicated by comparing the integrations of the ^{1}H NMR signals for free **3** (at δ = 1.6 ppm) and for bound **3** (at δ = 1.4 ppm, Scheme 9), or by comparing the signal of the methyl group in [**1**,**3**] (at δ = 2.2 ppm) with those of the two methyl groups in [**1**,**11**] (at δ = 2.45 ppm, Scheme 9). As it was the case for **3** (see above), **11** was quantitatively displaced from **1** by the addition of **2**.

All combined, these reactivities allow a sequence of double-exchange, displacement experiments to be performed on the basis of the knowledge of the equilibrium constants. First, the release of **11** by addition of **1** occurred within 1 h. Then, and although the equilibrium constant of formation of [**1**,**2**] is higher than about 10^8, the addition of **5** led to the full dissociation of this adduct in favour of that of **2** and **5**. The equilibrium constant for the formation of [**5**,**2**] is therefore at least 10^4 times higher than that of [**1**,**2**] and thus over 10^{12}, making the reaction appear as total. Finally, released **1** reacted with **11** already present in solution to give again an equilibrium with adduct [**1**,**11**] (Scheme 10).



Scheme 10. Double exchange illustrating sequential control of dynamic exchange events through the use of systems of increasing equilibrium constants.

Modulation of the Fluorescence of the Dynamic System

The dynamic features of the present processes allowed effective modulation of the anthracene fluorescence properties of the systems to be performed. In view of the temperature dependence of the equilibrium described above, in a solution of **1** and **3**, both at an initial concentration of 10 mM in chloroform, the concentration of free anthracene can be varied from 0.6 mM at 25 °C to 1.5 mM at 50 °C. This change might look rather small, but it is, however, enough to induce a tenfold decrease in the observed anthracene fluorescence upon increasing the temperature from 25 to 50 °C (Figure 1).

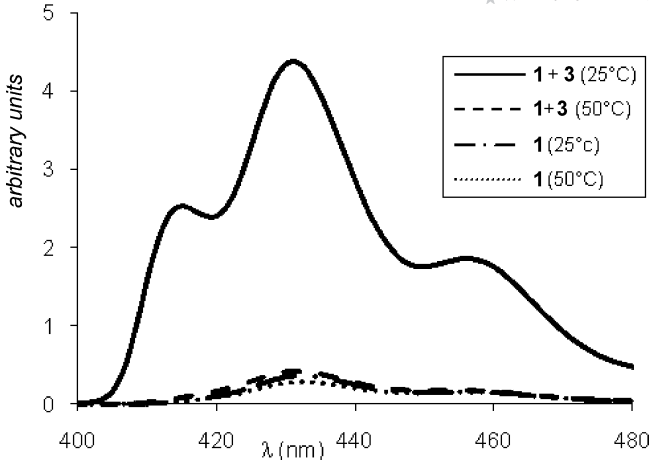


Figure 1. Fluorescence spectra of a 10 mM solution of **1** in $CHCl_3$ with or without addition of **3** (1 equiv.) at 25 and 50 °C. From bottom to top: **1** (50 °C), **1** (25 °C), [**1**+**3**] (50 °C), [**1**+**3**] (25 °C). Excitation at 395 nm, arbitrary units.

The high extent of change may be attributed to the intermolecular self-quenching of the fluorescence occurring in a solution of 9,10-dimethylanthracene above 0.1 M.[16] The fluorescence then decreases continually when the concentration increases, as can be seen from the integration over the whole visible spectra of the fluorescence intensity as a function of concentration (see Figure 2).

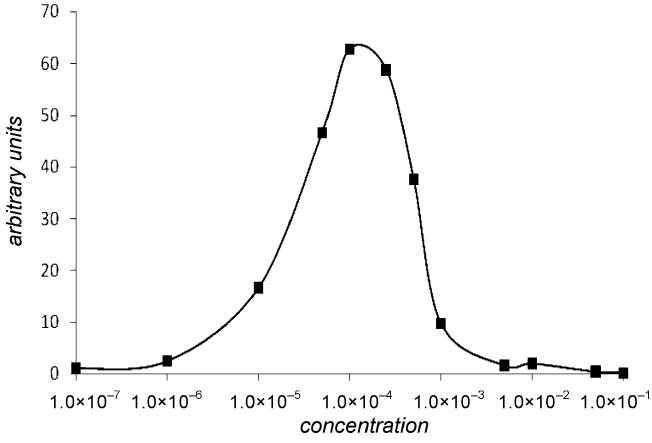


Figure 2. Spectral area by integration over the full fluorescence spectrum as a function of the concentration in 9,10-dimethylanthracene (**1**) alone in $CHCl_3$ (excitation at 395 nm, room temperature, arbitrary units, curve drawn through the points).

There is an increasing demand for devices permitting to sense analytes.[17] Photochemical devices are interesting systems due to their precise and easy readout. On the basis of the chemistry we developed for fulvenes and certain cyanoolefins,[4] a photochromic system gated by the Diels–Alder reaction, capable of sensing dienophiles, has been proposed.[18] The system described here can be seen as an anthracene-based thermally triggered fluorescent switch. The switch operates through a temperature change that modulates the fluorescence intensity of the anthracene through concentration change.

The reaction described in Scheme 1 can serve as basis for a sensor of dienes that react with tricyanoethylenecarboxylates, like cyclopentadiene or spiro[2.4]hepta-4,6-diene (**5**). Their introduction in the solution of adduct [**1**,**2**] will trigger a fluorescence signal through the release of 9,10-dimethylanthracene (**1**), and the amount released is proportional to the relative equilibrium constants.

Conclusions

The work reported here extends the systems displaying dynamic DA reactions at room temperature to the anthracene family of dienes and as well as to tricyanoethynylethylenes as dienophiles. Anthracenes were revealed to be a promising molecular optical device platform to work with owing to their fluorescent properties and amenability to further functionalization. Such functionalization provides opportunities to fine-tune the position of the dynamic DA equilibrium. The present system can also be considered as a means to chemically release a fluorescent anthracene derivative in solution, a feature that can be of useful application.

Experimental Section

General: All reagents were purchased from commercial suppliers and used without further purifications. THF was dried with sodium benzophenone ketyl. Preparative adsorption flash column chromatography was performed by using silica gel (Geduran, silica gel 230–400 mesh, Merck). 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectra were recorded with a Bruker Advance 400 spectrometer. The spectra were internally referenced to the residual solvent signal. The following notation is used for the splitting patterns: singlet (s), doublet (d), triplet (t). Electron impact (EI) mass spectra were performed by the Service de Spectrométrie de Masse, Institut de Chimie, Université Louis Pasteur. Electrospray (ESI and ESI-TOF) studies were performed with a Bruker Micro TOF mass spectrometer. Melting points were recorded with a Büchi Melting Point B-540 apparatus and are uncorrected. Microanalyses were performed at the Service de Microanalyse, Institut de Chimie, Université Louis Pasteur. Fluorescence spectroscopy was performed with a Jobin–Yvon Horiba Fluorolog 3.22 spectrometer. Solutions were made in $CHCl_3$ without degassing.

Analysis of the NMR Spectroscopic Data: Reversibility, component exchange or kinetics in the Diels–Alder reactions were studied by dissolving the diene (0.10 mmol) and dienophile in $CDCl_3$ (1.00 mL). The resulting solutions were placed in an NMR tube and spectra were taken at the desired temperature, after the required amount of time. For an exchange experiment, a second diene or dienophile component was added to the initial solution in stoichiometric amount or in excess. The proportions of library constituents were obtained simply by integration of the proton signals. The half-time of the process was estimated from evaluation of the end point on the basis of the time dependence of the formation and/or disappearance of a given reactant or adduct. Time-dependence curves are given as Supporting Information

Compounds 9,10-Dimethylanthracene (**1**), diethyl dicyanofumarate (**3**), 9-methylanthracene (**6**), anthracene (**7**), 9-cyanoanthracene (**9**) and 9,10-diphenylanthracene (**10**) were commercially available. Spiro[2,4]hepta-4,6-diene (**5**),[19] 9,10-dimethoxylanthracene (**8**),[20] 4-phenylbut-1-en-3-yne-1,2-tricarbonitrile (**11**),[12b] 2-cyano-3-{[4-(dimethylamino)phenyl]ethynyl}but-2-enedinitrile (**12**),[13] (*E*)-4-[4-(dimethylamino)phenyl]buta-1,3-diene-1,1,2-tricarbonitrile (**13**)[14] and 2-[4-(dimethylamino)phenyl]-1,1,2-tricyanoethylene (**14**)[14,21] were synthesized according to the procedure described in the literature. The following procedures were adapted from the literature.

***tert*-Butyl Tricyanoethylenecarboxylate (2):**[22] Tetracyanoethylene (6.0 g, 5.5 equiv.) was dissolved in dry THF (30 mL) at 70 °C. *tert*-Butyl cyanoacetate (1.7 g, 8.5 mmol) was added followed by pyridine (100 μL, cat.), which caused the reaction mixture to become dark. The mixture was heated at reflux for 40 h. Afterwards, it was cooled down to room temperature and then diluted with chloroform (50 mL) and pentane (100 mL). The mixture was allowed to stand for 1 h, causing a black tarry phase to settle out and part of the excess amount of tetracyanoethylene to precipitate. The precipitate was filtered off, and the filtrate was washed repeatedly with water until the organic layer became a light red/purple colour. It was then dried with magnesium sulfate and concentrated until a precipitate started to form. It was filtered and heptane (50 mL) was added, and then the solution was concentrated again. When a precipitate started to form, the solution was cooled to 0 °C, and the formed white solid was filtered off. If necessary, this solid was crystallized in chloroform/pentane (1:9). This operation was repeated until the ^{13}C NMR spectrum showed no trace of tetracyanoethylene. The product was obtained as a white powder (708 mg). The product must be stored at –30 °C. Yield: 41%. M.p. 102–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.65 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5 [-*C*(=O)O-], 133.8 [C=*C*(-CN)-C(=O)-], 111.0, 109.6, 108.6 (3×-C≡N), 106.6 [C=*C*(-CN)$_2$], 69.9 (O-*C*=C), 27.6 (O-C-*C*) ppm. MS (EI): *m*/*z* = 130.1 [M – *o*-*t*Bu]$^+$. $C_{10}H_9N_3O_2$ (203.20): calcd. C 59.11, H 4.46, N 20.68; found C 59.10, H 4.03, N 22.15.

Bis(2-methoxyethyl) Dicyanofumarate (4):[23] To a solution of 2-methoxyethylcyanoacetate (7.2 g, 50 mmol) in THF (25 mL) was added thionyl chloride (14.5 mL, 4 equiv.). The mixture was heated at reflux under an inert atmosphere for 4 h, and afterwards, by cooling to room temperature, the product started to precipitate. This precipitation was enhanced by cooling the reaction mixture to 0 °C and adding cyclohexane (10 mL). The solid was filtered, washed with H_2O and dried under reduced pressure. The product was obtained as a white solid after crystallization in 2-propanol (3.4 g). Yield: 61%. M.p. 109–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.58 [t, ^3J(H,H) = 4.2 Hz, 4 H], 3.75 [t, ^3J(H,H) = 4.2 Hz, 4 H], 3.43 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.6 [-*C*(=O)O-], 125.8 (*C*=*C*), 111.1 (-C≡N), 69.3 [C(=O)O-*C*-C-O], 67.5 (-C-*C*-O-C), 59.1 (O-*C*) ppm. MS (ESI-TOF): *m*/*z* (%) = 305.0757 (100) [M + Na]$^+$. $C_{12}H_{14}N_2O_6$ (282.25): calcd. C 51.06, H 5.00, N 9.93; found C 50.43, H 4.95, N 9.66.

2-(4-Nitrophenyl)-1,1,2-tricyanoethylene (15):[22] 4-Nitrophenylacetonitrile (1.7 g, 10.4 mmol) and tetracyanoethylene (3.3 g, 2.5 equiv.) were dissolved in dry THF (50 mL). The solution was heated to 60 °C and pyridine (1 mL) was added. The solution was heated to reflux under an inert atmosphere for 16 h. Afterwards, it was diluted with chloroform (20 mL) and pentane (100 mL) and left to stand for 1 h. The precipitated tetracyanoethylene was filtered, and the filtrate was evaporated. Chromatography (SiO_2; ethyl acetate/cyclohexane, 1:1) gave **15** as a yellow solid (701 mg). Yield: 30%. M.p. 90–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 [d, ^2J(H,H) = 8.8 Hz, 2 H], 8.19 [d, ^2J(H,H) = 8.8 Hz, 2 H] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.0 (O_2N-C_{Ar}), 139.8, 133.2,

[=*C*(-CN)-C_{Ar} + C=C(-CN)-C_{Ar}], 130.7, 124.7 (2 C_{Ar}-H), 113.1, 110.4, 110.1 (3 -C≡N), 97.0 [C=*C*(-CN)$_2$] ppm. $C_{11}H_4N_4O_2$ (224.18): calcd. C 58.94, H 1.80, N 24.99; found C 59.15, H 1.89, N 25.23.

Supporting Information (see also the footnote on the first page of this article): NMR spectra of the equilibria and kinetic studies.

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