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Thermally reversible novel photochromic dihydroindoles

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ABSTRACT: Thermally reversible novel photochromic 4,5- and 6,7-dihydroindoles possessing a hexafluoropropano-bridge, a spiro-adamantane moiety and a phenyl group were synthesized and their photochemical forward as well as thermal back reactions were investigated. While the open coloured form of 4,5-dihydroindole had an absorption maximum at 417 nm in toluene, that of 6,7-dihydroindole at 553 nm. Although the thermal back reaction of the former took about 2 h at r.t., that of the latter completed within a few minutes. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: photochromism; thermally reversible; dihydroindole; perfluorocyclopentene; adamantane

INTRODUCTION

Photochromic compounds[1] are divided into two categories. One is thermally irreversible, the other thermally reversible. While the former includes only limited families such as fulgides[2] and diarylethenes,[3] the latter includes a number of classes such as spiropyrans[4] and spirooxazines,[4] naphthopyrans (chromens),[5] azobenzenes,[6] hexaarylbisimidazoles,[7] stilbenes[8] and so on. Although some of the latter – spirooxazines and naphthopyrans – have already been used for the auto light-regulating ophthalmic lenses,[5] the number of photochromic families used for practical applications is so small.

In the previous papers, we introduced new thermally reversible photochromic dihydrobenzothiophenes (DHBTs)[9,10] (**1** and **2**) and dihydronaphthalenes (DHNPs)[10] (**3**–**6**) with a hexafluoropropano-bridge, a spiro-adamantane group and a phenyl group (Scheme 1). They showed thermally reversible photochromism based on 6π-electrocyclization (Scheme 2). However, the decolouration rate was so slow for **1** and **2**, and so fast for **3**–**6** that the way of application of them would be restricted. In this paper, the synthesis and photochromic reactions of dihydroindoles (DHINs; **7** and **8**) are described. Both of them showed thermally reversible photochromic reactions, and the colouration of one of the isomers **7** was strong and fast and the decolouration was reasonably quick.

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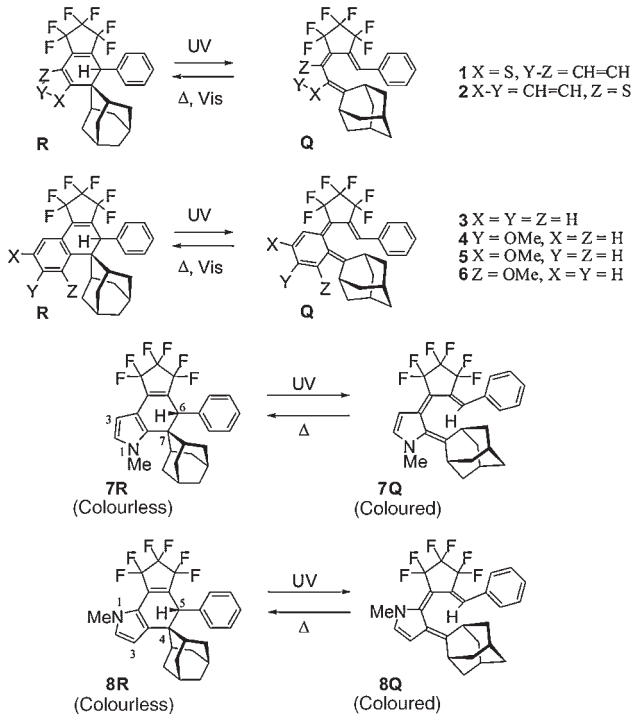
RESULTS AND DISCUSSION

Molecular design

In the previous papers, we described the synthesis of dihydroaromatic molecules which show photochromic reactions. They can be produced as the open form (O-form) possessing a 2,2,3,3,4,4-hexafluorocyclopentene with an aromatic ring on its C-1 and the 1-adamantylidene-1-phenylmethyl group on C-2. Upon UV-light irradiation, it cyclizes to form the closed form (C-form) by the 6π-electrocyclization, which, in order to restore the aromaticity, changes to the rearranged form (R-form) by the thermal 1,5-sigmatropic hydrogen rearrangement. The thermally reversible photochromism occurs between the R-form and the coloured quinodimethane form (Q-form). Irradiation of UV light to the colourless R-form generates the coloured Q-form. The Q-form goes back to the R-form thermally as well as by visible-light irradiation. When the quantum yield of the colouring reaction is large and back reaction is small, and the thermal back reaction is quick, the compound would show a strong colour under the sunlight which contains both UV and visible lights, but it becomes colourless quickly when the light is shaded.

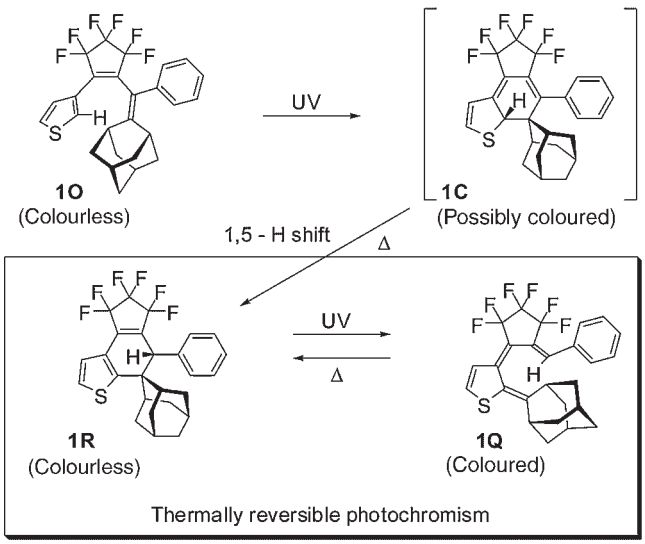
We have already reported the synthesis of DHBTs **1** and **2** and DHNPs **3**–**6**. The approximate time required for



Scheme 1. Photochromism of dihydroaromatic compounds

the Q-forms to change to the R-forms is listed in Table 1. DHBTs take hours, while DHNPs take less than a second at room temperature.

When the R-forms of DHBTs and DHNPs become their Q-forms, the thiophene or benzene rings open to generate quinodimethane-type structures. In this occasion, they loose the aromaticity. It is easily assumed that when the aromatic stabilization energy (ASE) of the R-form is larger, the corresponding Q-form is more unstable. It would make the activation energy of the thermal back reaction smaller, and the decolouration takes place faster.



Scheme 2. Photochromism of dihydrobenzothiophene

Table 1. Decolouration time (Q-form to R-form) at r.t.

	1[a]	2[a]	3[b]	4[b]	5[b]	6[b]
Decolouration time	2.5 h	>6 h	<1 s	<1 s	<1 s	<1 s

[a] In toluene solution.
[b] In amorphous polyolefin film.

Katritzky *et al.*[11] reported the calculation-based ASE of heteroaromatic compounds. Some of their data are shown in Table 2.

There is a strong relationship that when the ASE is smaller (thiophene: DHBT), the thermal back reaction proceeds at a slow rate, and the ASE is larger (benzene: DHNP), the thermal back reaction occurs instantaneously. In order to obtain a thermally reversible photochromic compound whose colour disappears within several minutes or so while it exhibits certain coloration, we have to look for an aromatic ring whose ASE is in between them. We found that the ASE of pyrrole is 106.6 kJ mol^{-1} which is ideal for our purpose. Thus, we decided to synthesize DHINs **7** and **8**.

Synthesis of 7 and 8

Synthetic pathways of **7** and **8** are shown in Scheme 3.

Regioselective bromination reactions of 1-methylpyrrole (**9**) to form 3-bromo-1-methylpyrrole (**10**) and 2-bromo-1-methylpyrrole (**11**) were carried out according to the reported procedures by NBS in tetrahydrofuran (THF) and by NBS with a catalytic amount of PBr_3 in THF, respectively.[12] Lithiation of bromopyrroles **10** and **11** with butyllithium followed by the reaction with 1-(1-adamantyliene-1-phenylmethyl)-2,3,3,4,4,5,5-heptafluorocyclopentene[9] afforded **7O** and **8O** in 12% and 11% yield, respectively. Irradiation of **7O** with 313-nm light in cyclohexane or toluene gave, after 6π-electrocyclization followed by hydrogen rearrangement, **7R** in 11%. Similarly, irradiation of **8O** with 313-nm light in toluene gave **8R** in 57% yield.

Photocolouration and thermal decolouration of 7R and 8R

For the compounds **1R–6R**, the colourless R-form generates the coloured Q-form by UV irradiation, which goes back to the R-form thermally. We envisioned the similar reactions. Upon irradiation of 366-nm light at 24 °C, the toluene solution of **7R** changed from colourless to purple. The absorption maximum was 553 nm. Apparently the coloured **7Q** was formed. When the coloured solution was left in the dark, the purple colour disappeared completely within 5 min. The spectral changes during UV irradiation and thermal decolouration of **7** are shown in Figs 1 and 2, respectively.

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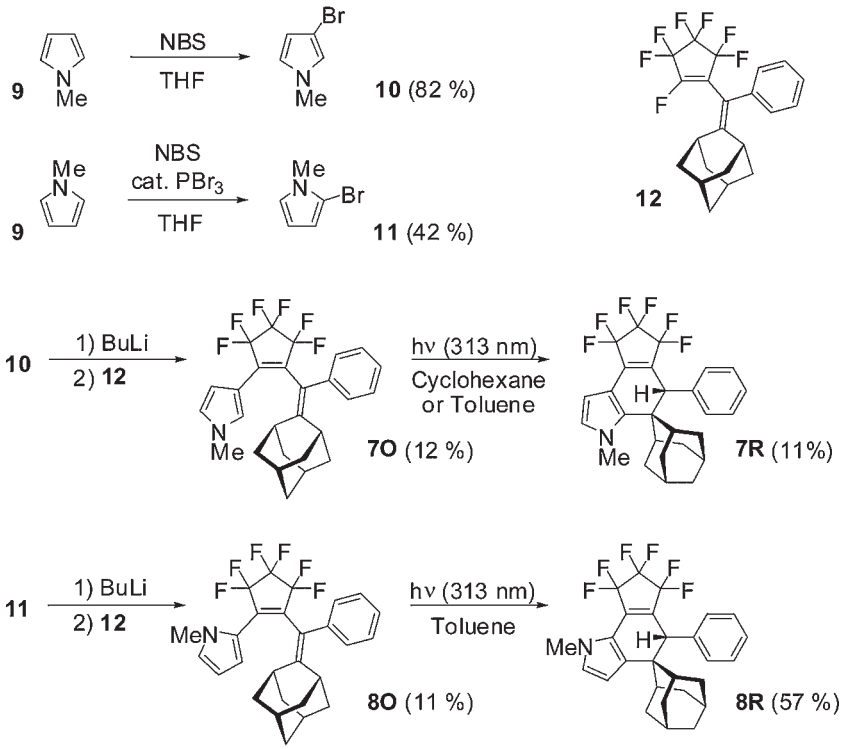
Table 2. Aromatic stabilization energy[11]

Aromatic stabilization energy/kJ mol^{-1}	Thiophene	Benzene	Pyrrole
	93.6	111.6	106.6



Scheme 3. Synthesis of dihydroindoles

Similarly, the toluene solution of **8R** was irradiated with 313-nm light at 26.2 °C. The solution turned from almost colourless to yellow, and the absorption maximum of the new band ascribable to the formation of **8Q** was 417 nm. Different from **7Q**, the decolouration of **8Q** took much longer time. The change in absorption spectra of coloration and decolouration of **8** are shown in Figs 3 and 4, respectively.

Although the absorption spectrum of **7** (**7R**) before UV irradiation in Fig. 1 was identical with that after the complete thermal back reaction from **7Q** in Fig. 2 that of **8** after the thermal back reaction in Fig. 4 was not identical with the spectrum before UV irradiation (Fig. 3). One of the reasons should be the difference of the wavelength of the irradiation energy. While the irradiation on **7R** was carried out with 366-nm light of mercury lamp, 313-nm

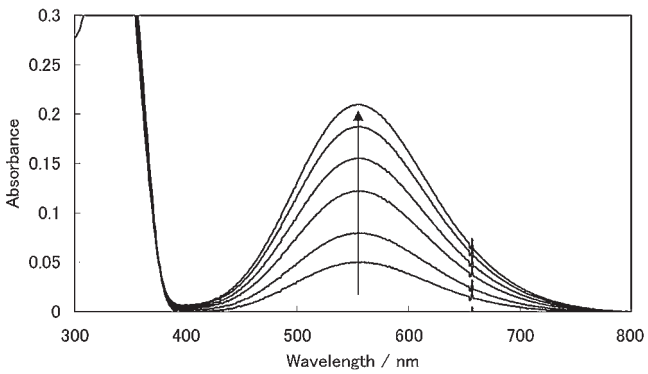


Figure 1. Change in absorption spectra of **7R** in toluene at 24 °C (2.02×10^{-4} mol dm^{-3}). Irradiation time/s; 0, 10, 20, 40, 60, 100, 200. Light intensity; 0.94 mW cm^{-2} (366 nm). Cell length; 1 cm

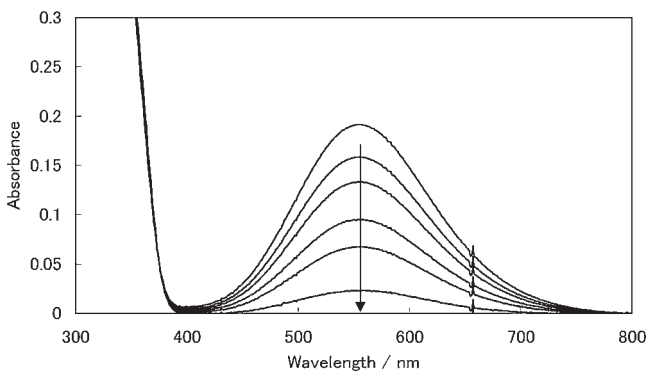


Figure 2. Change in absorption spectra of **7Q** in toluene at 24 °C (2.02×10^{-4} mol dm^{-3}). Elapsed time/s; 0, 10, 20, 40, 60, 120, 300. Cell length; 1 cm

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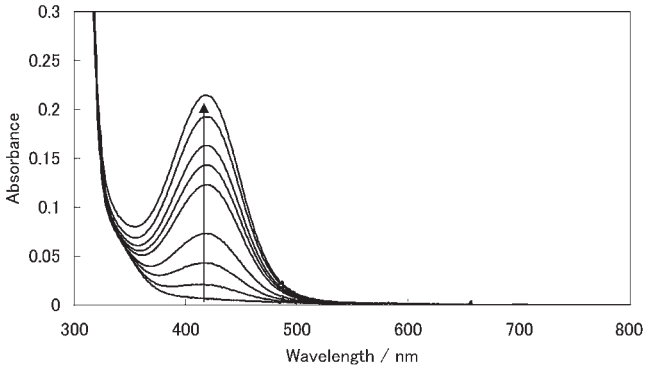

Figure 3. Change in absorption spectrum of **8R** in toluene at 26 °C (1.00×10^{-4} mol dm^{-3}). Irradiation time/s; 0, 20, 60, 120, 240, 300, 420, 600, 960. Light intensity; 0.68 mW cm^{-2} (313 nm). Cell length; 1 cm

light was used for **8R** because **8R** does not have a large absorption at 366 nm. The use of 313-nm light might have caused degradation of **8** to some extent to generate some slightly coloured species.

In the case of DHBTs **1** and **2**, the decolouration from **2Q** to **2R** (4,5-dihydrobenzothiophene)[10] was slower than that from **1Q** to **1R** (6,7-dihydrobenzothiophene).[9] The similar phenomenon occurred for **7** and **8**. Namely, **8Q**–**8R** (4,5-dihydroindole) was slower than **7Q**–**7R** (6,7-dihydroindole).

We then obtained the reaction rate constants of thermal reactions of **7Q** and **8Q** at different temperatures. The reaction kinetics was expressed by the sum of two first-order reactions; a fast but less dominant (28–6%) one and a slow and dominant (94–72%) one. The Arrhenius activation energies (E_a) and frequency factors (A) of the slower thermal decolouration reactions were then calculated. The results are listed in Table 3, together with the data of **1Q** and **2Q**. The data show that the largeness of reaction rate constants of **7Q** is basically attributed to the small E_a. However, although E_a of **8Q** is smaller than that of **7Q**, it is compensated by its much smaller frequency factor.

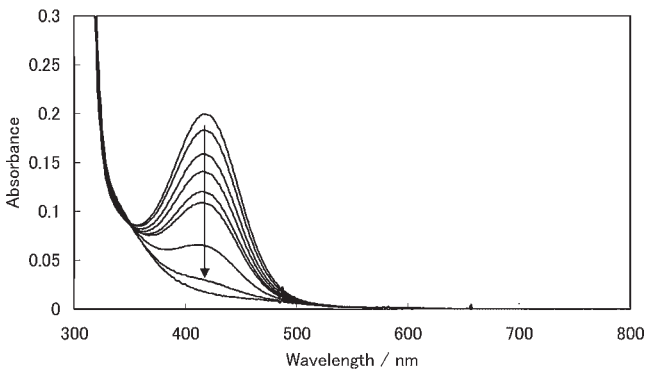

Figure 4. Change in absorption spectra of **8Q** in toluene at 26 °C (1.00×10^{-4} mol dm^{-3}). Elapsed time/s; 0, 60, 180, 300, 480, 600, 1200, 2400, 4800. Cell length; 1 cm

The structures of the Q-forms generated from **7R** and **8R**, which exhibit different decolouration rates, may be the E/Z isomers of the benzylidene moiety attached to the hexafluorocyclopentane ring of the Q-form. During the photochemical ring opening of the R-form, the cyclohexadiene ring opens by way of the conrotatory mode, which can give the geometrical isomers of the double bond. However, it is not certain which isomer corresponds to the faster-reacting one and the slower-reacting one.

The absorption maxima of the Q-forms of 4,5-dihydro derivatives are shorter than that of 6,7-dihydro derivatives. It is attributed to the longer conjugation of 6,7-dihydro derivatives as shown in Scheme 4. It is reasonable that the absorption maximum of **7Q** is longer than that of **1Q** because of the stronger electron donating ability of the nitrogen atom than the sulphur atom. However, it is interesting that the absorption maximum of **8Q** is shorter than **2Q**. It may be attributed to the steric congestion caused by the methyl group on nitrogen atom and the perfluorocyclopentene ring which would have generated the torsion, that is, deviation from the planarity, of the conjugation system.

In conclusion, we have synthesized new thermally reversible photochromic 6,7- and 4,5-dihydroindoles (**7R** and **8R**, respectively) possessing a hexafluoropropano-bridge, a spiro-adamantane moiety and a phenyl group. While the coloured Q-form of **8R** had an absorption maximum at 417 nm in toluene, that of **7R** at 553 nm. The difference in the absorption maxima was explained by the difference in the length of conjugation and the steric congestion around the conjugation system. Although the thermal back reaction of **8Q** took more than 1 h at r.t. that of **7Q** completed within a few minutes.

EXPERIMENTAL

General

^{1}H NMR spectra were recorded with JEOL JNM-EX-270 (270 MHz) spectrometer and JNM-AL-400 (400 MHz) spectrometer in $CDCl_3$. The signals are expressed as parts per million down field from tetramethylsilane, used as an internal standard (δ value). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; m, multiplet. IR spectra were measured using a HORIBA FT-730 spectrometer. Low- and high-resolution mass spectra were taken with a JEOL JMS-AX-600 mass spectrometer. UV–Vis spectra were recorded on a JASCO V-550 UV–Vis spectrometer or a Shimadzu Multispec-1500 UV–Vis spectrometer. The emission line of 313 nm of a 500 W high-pressure mercury lamp (Ushio electric) was separated by filters (5 cm water filter, a UV-D35 glass filter, 5 cm aqueous $NiSO_4 \cdot 6H_2O$ solution, 1 cm aqueous K_2CrO_4–NaOH solution and 1 cm aqueous potassium hydrogenphthalate solution). The emission line of 366 nm of a 500 W high-pressure mercury lamp (Ushio electric) was sepa-

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Table 3. Absorption maximum and kinetic data of decolouration of Q-forms in toluene

	λ_{max} (nm)	T (K)	k (s^{-1})		E_a (kJ mol^{-1})	A (s^{-1})
		290	1.33×10^{-4}			
1Q	500	299	4.73×10^{-4}		84.0	1.96×10^{11}
		310	1.23×10^{-4}			
		302	9.68×10^{-5}			
2Q	468	306	1.85×10^{-4}		106.3	2.50×10^{14}
		315	6.05×10^{-4}			
		289	2.61×10^{-2}	4.18×10^{-3}		
7Q	537	298	1.07×10^{-1}	1.17×10^{-2}	79.5[b]	9.93×10^{11} [b]
		308	6.51×10^{-1}	3.38×10^{-2}		
		289	7.49×10^{-4}	9.86×10^{-5}		
		294	1.39×10^{-3}	1.66×10^{-4}		
8Q	417	298	3.23×10^{-3}	3.18×10^{-4}	73.1[b]	2.40×10^{9} [b]
		308	—[a]	5.72×10^{-4}		
		309	9.27×10^{-3}	7.91×10^{-4}		

[a] Not observed.
[b] Values for the slower reactions.

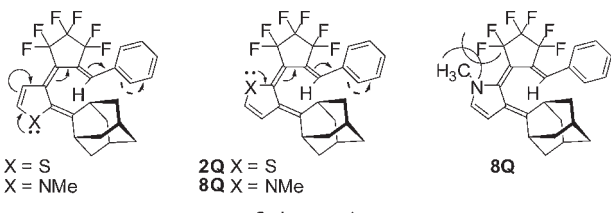
rated by filters (5 cm water filter, 5 cm aqueous $CuSO_4$ solution, a UV-35 glass filter and a UV-D35 glass filter). The silica-gel column chromatographic separation was carried out with a Merck Kieselgel 60 (230–400 mesh) with ethyl acetate and hexane as an eluant. The alumina column chromatographic separation was carried out with a Merck Aluminium oxide 90 active basic (70–230 mesh) with ethyl acetate and hexane as an eluant. Analytical thin-layer chromatography was performed on Merck pre-coated silica gel 60 F-254, 0.25 mm thick TLC plates. All of the synthetic reactions were carried out under a dry nitrogen atmosphere. THF was freshly distilled from benzophenone ketyl.

Synthesis of 1-(adamantylidene-1-phenylmehyl)-3,3,4,4,5,5,-hexafluoro-2-(1-methyl-3-pyrryl)cyclopentene (7O)

To a solution of 3-bromo-1-methylpyrrole (**10**,[12] 213 mg, 1.33 mmol, 5.3 eq.) in 10 ml THF at −60 °C was added TMEDA (0.25 ml, 1.68 mmol, 6.7 eq.) and a hexane solution of butyllithium (1.52 mol dm^{-3}, 1.1 ml, 1.67 mmol, 6.7 eq.), and the mixture was stirred for 90 min at that temperature. This mixture was added dropwise to a THF (4.0 ml) solution of **12** (104 mg, 0.250 mmol, 1 eq.) at −60 °C, and the resulting mixture was kept stirring over night. After the reaction was quenched with water, the mixture was extracted with ethyl acetate three times. The organic layer was washed with saturated brine, and dried with anhydrous sodium sulphate. After the drying agent was filtered off, the solvent was removed *in vacuo*. The residue was purified by silica-gel column chromatography to give **7O** (78.9 mg, 12%). Mp 145–147 °C. IR (KBr) ν cm^{-1}: 3133, 3081, 2948, 2929, 2914, 2853, 1635, 1610, 1450, 1427, 1366, 1337, 1303, 1277. ^{1}H NMR (270 MHz, $CDCl_3$) 1.5–2.2 (12H, m), 2.59 (1H, s), 3.09 (1H, s), 3.69 (3H, s), 6.62 (1H, dd, J/Hz = 2.6, 2.0), 6.81 (1H, dd, J/Hz = 2.6, 2.0), 7.2–7.3 (6H, m). MS (EI, 70 eV) *m/z* 477 (M^+, 100), 356 (11). Found: *m/z* 477.18735. Calcd for $C_{27}H_{25}F_6N$: M, 477.18910

Synthesis of 1-(adamantylidene-1-phenylmehyl)-3,3,4,4,5,5,-hexafluoro-2-(1-mehyl-2-pyrryl)cyclopentene (8O)

To a solution of 2-bromo-1-methylpyrrole (**11**,[12] 696 mg, 4.35 mmol, 4.6 eq.) in 50 ml THF at −73 °C was added a hexane solution of butyllithium (1.60 mol dm^{-3}, 3.3 ml, 5.3 mmol, 5.6 eq.), and the mixture was stirred for 60 min at that temperature. This mixture was added dropwise to a THF (6.4 ml) solution of **12** (395 mg, 0.949 mmol, 1 eq.) at −73 °C, and the resulting mixture was kept stirring over night. After the reaction was quenched with water, the mixture was extracted with ethyl acetate three times. The organic layer was washed with saturated brine, and dried with anhydrous sodium sulphate. After the drying agent was filtered off, the solvent was removed *in vacuo*. The residue was purified by silica-gel column chromatography to give **8O** (234 mg, 11%). Mp 107–110 °C. IR (KBr) ν cm^{-1}: 3084, 3024, 2938, 2883, 2854, 1612, 1599, 1374, 1281. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.7–2.0 (12H, m), 2.63 (2H, br s), 3.25 (3H, s), 6.14 (1H, dd, J/Hz = 3.3, 2.6), 6.35 (1H, dd, J/Hz = 3.3, 2.0), 6.67 (1H, dd, J/Hz = 2.6, 2.0), 6.96 (2H, m), 7.2 (3H, m). MS (EI, 70 eV)



Scheme 4. Conjugation in Q-forms.

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m/z 477 (M^+, 100), 223 (54). Found: *m/z* 477.18777. Calcd for $C_{27}H_{25}F_6N$: M, 477.18910.

Synthesis of 4′,5′-Hexafluoropropano-1-methyl-6′-phenylspiro[adamantine-2,7′(6′H)-indole] (7R)

A solution of **7O** (30.7 mg, 0.064 mmol) in cyclohexane (*ca* 80 ml) was irradiated with 313-nm light for 21 h. Similarly, a solution of **7O** (51.2 mg, 0.107 mmol) in toluene (*ca* 80 ml) was irradiated with 313-nm light for 25 h. Each solution was kept in the dark for 1 day, and the solvent was removed *in vacuo*. The residue was combined and purified by aluminium oxide column chromatography, to give **7R** (8.74 mg, 11%). Mp 190–194 °C. IR (KBr) $\nu\,cm^{-1}$: 3001, 2946, 2926, 2912, 2856, 1452, 1394, 1358, 1316, 1249. ^1H NMR (270 MHz, $CDCl_3$) δ 1.3–2.5 (13H, m), 2.54 (1H, d, J/Hz = 13.2), 3.45 (3H, s), 4.44 (1H, d, J/Hz = 4 .0 (H–F coupling)), 6.40 (1H, dd, J/Hz = 3.3, 1.3 (H—F coupling)), 6.57 (1H, d, J/Hz = 3.3), 6.64 (2H, d, J/Hz = 7.3), 7.12 (2H, t, J/Hz = 7.3), 7.19 (1H, t, J/Hz = 7.3). MS (EI, 70 eV) *m/z* 477 (M^+, 100), 386 (66), 330 (22). Found: *m/z* 477.19061. Calcd for $C_{27}H_{25}F_6N$: M, 477.18910.

Synthesis of 6′,7′-Hexafluoropropano-1-methyl-5′-phenylspiro[adamantane-2,4′(5′H)-indole] (8R)

A solution of **8O** (20.7 mg, 0.0434 mmol) in toluene (*ca* 80 ml) was irradiated with 313-nm light for 4.5 h. The resulting solution was kept in the dark for 1 day, and the solvent was removed *in vacuo*. The residue was purified by aluminium oxide column chromatography to give **8R** (11.8 mg, 57%). Mp 124–128 °C. IR (KBr) $\nu\,cm^{-1}$: 3089, 3067, 3028, 2941, 2894, 2853, 1450, 1419, 1369, 1345, 1298. ^1H NMR (400 MHz, $CDCl_3$) δ 1.4–1.7 (9H, m), 1.73 (1H, s), 2.06 (2H, b s), 2.18 (2H, d, J/Hz = 7.3), 3.44 (3H, s), 6.13 (1H, d, J/Hz = 2.9), 6.71 (1H, d, J/Hz = 2.9), 6.71 (2H, d, J/Hz = 7.3), 7.09 (1H, d, J/Hz = 2.4 (H—F coupling)), 7.11 (2H, t, J/Hz = 7.3), 7.20 (1H, t, J/Hz = 7.3). MS (EI, 70 eV) *m/z* 477 (M^+, 6), 476 (30), 475 (100), 352 (37). Found: *m/z* 477.19080. Calcd for $C_{27}H_{25}F_6N$: M, 477.18910.

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