Electronic Supplementary Information: Photochrome-doped organic films for photonic keypad locks and multi-state fluorescence

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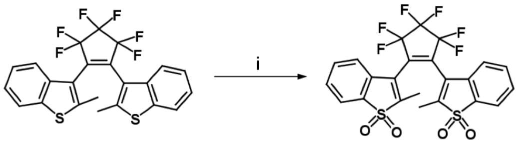
S1. Synthesis of P1.



Scheme: Synthetic route to P1. Reagents and conditions: (i) 3-Chloroperbenzoic acid, CH_2Cl_2, r.t., 24 hrs.

Materials: 1,2-bis(2-methyl-1-benzothiophene-3-yl)hexafluorocyclopentene (Tokyo Chemical Industry), 3-chloroperoxybenzoic acid (Sigma-Aldrich), dichloromethane (Unilab), hexane (ACI Labscan), ethyl acetate (ACI Labscan), sodium sulphate (Unilab) and magnesium sulphate (Chem-supply).

Instrumentation: Flash chromatography was performed on a Grace Reveleris X2 system using the Reveleris Navigator software package. NMR spectra were recorded on a Varian 400 MHz spectrometer.

Synthesis:[1] 1,2-bis(2-methyl-1-benzothiophene-3-yl)hexafluorocyclopentene (50 mg, 0.107 mmol) and 70% 3-chloroperoxybenzoic acid (145 mg, 0.59 mmol) were dissolved in dichloromethane (2.5 mL) and stirred for 24 h at room temperature in the dark. The solution was then washed with saturated Na_2SO_4, the organic layer separated, dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (pre-packed, 4 gram HP-silica, hexane:ethylacetate = 4:1) yielded 1,2-bis(2-methyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (P1). Due to the small scale of our reaction, we found that the chromatography method was unable to remove a m-chlorobenzoic acid impurity from the P1 sample (see Figure 1). The concentration of the P1 solution used to prepare the PMMA films was corrected using the known molar absorption coefficient of P1 (o-BTFO4).[1] This solution contained 0.15 mM P1 and 1.30 mM m-chlorobenzoic acid, with the reaction yield of P1 inferred to be 16%. The photophysical properties of the photochrome-doped films are not affected by the presence of m-chlorobenzoic acid, as it only absorbs UV light at wavelengths shorter than those employed in our experiment ($\lambda_{irr} = 320\,\text{nm}$) (see Figure 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, J = 7.3 Hz, 2H), 7.72 (d, J = 7.3 Hz, 2H), 7.64-7.54 (m, 4H), 7.64-7.54 (m, 4H), 7.49-7.43 (m, 4H), 7.14 (d, J = 7.5 Hz, 4H), 2.20 (s, 3H), 2.04 (s, 3H).

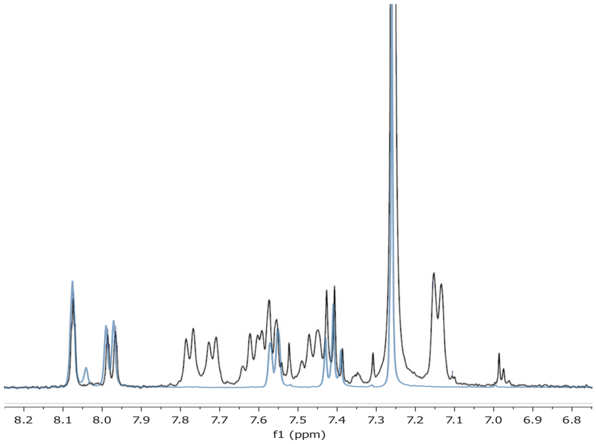


Figure 1: NMR spectrum of the P1 sample (black line). When taking into account the impurity due to m-chlorobenzoic acid (blue line), the remaining resonances match those reported for the P1 (o-BTFO4) photochrome.[1]

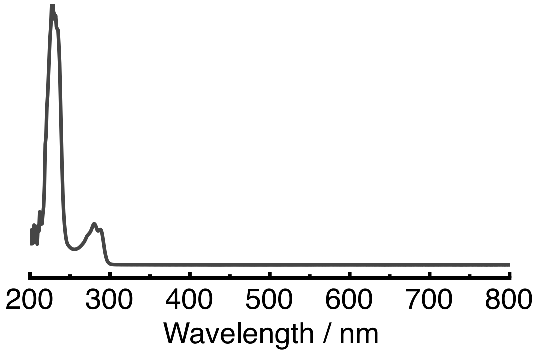
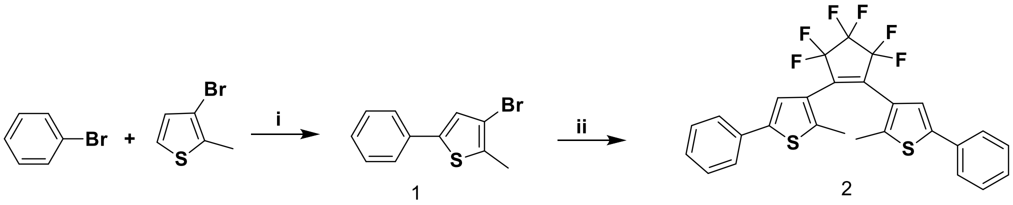


Figure 2: Absorption spectrum of m-chlorobenzoic acid.

S2. Synthesis of P2.



Scheme: Synthetic route to P2. Reagents and conditions: (i) $Pd(OAc)_2$, K_2CO_3, pivalic acid, dimethylacetamide, 100 °C, Ar, 18 h. (ii) n-butyllithium (1.45 M), tetrahydrofuran, -78 °C; then octafluorocyclopentene, -78 °C to r. t. overnight.

Materials: 2-methyl-3-bromothiophene (Combi Blocks), bromobenzene (Sigma Aldrich), palladium acetate (Sigma Aldrich), potassium carbonate (Univar), pivalic acid (Sigma Aldrich), dimethylacetamide (Sigma Aldrich), petroleum ether (Ajax Finechem), toluene (Univar), diethyl ether (Fisher Scientific), n-butyllithium (Sigma Aldrich), tetrahydrofuran (Unichrome), octafluorocyclopentene (Synquest Labs) were used as received.

Instrumentation: NMR spectra were recorded on a Bruker AscendTM 400 MHz spectrometer.

3-Bromo-2-methyl-5-phenylthiophene (1):[2,3] A stirred solution of 2-methyl-3-bromothiophene (3.54 g, 20 mmol), bromobenzene (3.14 g, 20 mmol), pivalic acid (0.8 g, 8 mmol) and potassium carbonate (6.60 g, 48 mmol) in dimethylacetamide (40 cm^3) was purged with argon for 20 min. To this solution palladium acetate (0.122 g, 4 mol) was added prior to purging for a further 5 min. The reaction mixture was heated at 100 °C for 18 h then allowed to cool to room temperature. Water (200 cm^3) was added to the reaction mixture prior to extracting with diethyl ether (2 x 150 cm^3). The combined ether extract was washed with brine (2 x 100 cm^3) and dried over Na_2SO_4 prior to the removal of the solvent. The product was purified by column chromatography over silica gel using petroleum ether as the eluent which afforded the product as a white solid (2.9 g, 58%). ^1H NMR (400 MHz, $CDCl_3$) δ: 2.42 (s, 3H), 7.11 (s, 1H), 7.28-7.30 (m, 1H), 7.34-7.39 (m, 2H), 7.49-7.52 (m, 2H).

1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (2):[4] n-BuLi (6.76 mmol) was added dropwise to a stirred solution of 3-bromo-2-methyl-5-phenylthiophene (1.58 g, 6.76 mmol) in dry THF (30 cm^3) at -78 °C. The reaction was stirred for 1 h prior to the slow addition of octafluorocyclopentene (0.42 cm^3, 3.21 mmol). This reaction mixture was stirred for 2 h at -78°C prior to slowly warming to room temperature overnight. The reaction was quenched with HCl (3M, 15 cm^3) followed by extraction with diethylether (3 x 15 cm^3) and washed with water (3 x 15 cm^3) prior to drying over $MgSO_4$ and the removal of the solvent under vacuum. The product was purified by column chromatography over silica gel using petroleum ether as the eluent which afforded the product (P2) as a blue solid (0.740 g, 44%). ^1H NMR (400 MHz, $CDCl_3$) δ: 1.98 (s, 6H), 7.28 (s, 2H), 7.30-7.32 (m, 2H), 7.37-7.40 (m, 4H), 7.54 (m, 4H).

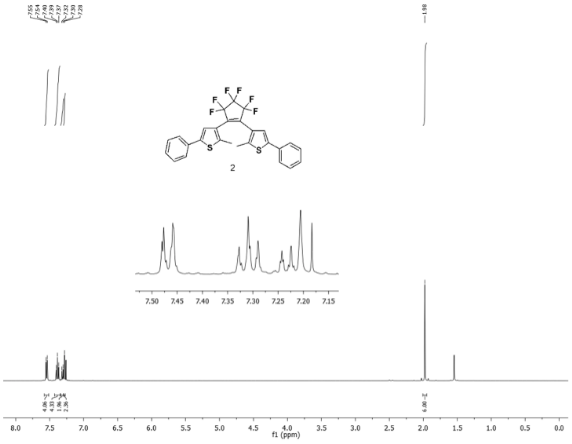


Figure 3: NMR spectrum of P2.

S3. Statistical average FRET donor-acceptor distance.

To calculate the statistical average distance (D_{D-A}) between a FRET donor and the nearest FRET acceptor neighbor, we use the following equation:

$$D_{D-A} = 0.554 \times {n_A}^{-(\frac{1}{3})} \tag{1}$$

where n_A is the number of FRET acceptor molecules per volume unit.[5]

S4. Time-resolved fluorescence decay fitting.

The fluorescence decay curve of c-BTFO4 in chloroform solution was fitted using a biexponential decay function:

$$I(t) = A_1 e^{-(\frac{t}{\tau_1})} + A_2 e^{-(\frac{t}{\tau_2})} \tag{2}$$

where A_1 and A_2 are the amplitudes for the first and second decay components, respectively, and τ_1 and τ_2 are the lifetimes for the first and second decay components, respectively.

The fluorescence decay curve of c-BTFO4 in the PMMA matrix was fitted using a single exponential decay function:

$$I_D(t) = A e^{-(\frac{t}{\tau})} \tag{3}$$

where A is the amplitude and τ is the lifetime.

When introducing the FRET acceptors into the PMMA matrix (randomly distributed in three dimensions), the fluorescence decay of the FRET donor will become faster and non-exponential due to the introduction of the FRET decay channel.[6] The fluorescence decay curve of the c-BTFO4 FRET donor in the PMMA matrix, in the presence of the FRET acceptor, was fitted using a stretched exponential decay function:

$$I_{DA}(t) = A\,e^{-\left(\frac{t}{\tau_c}\right)^{\beta}}, \tag{4}$$

where A is the amplitude, τ_c is the characteristic lifetime, and β is the dispersion parameter. Fitted parameters were used to determine the average lifetime, τ:

$$\tau = \frac{\tau_c}{\beta}\Gamma\left(\frac{1}{\beta}\right)$$

$$\Gamma\left(\frac{1}{\beta}\right) = \int_0^{\infty} x^{\frac{1}{\beta}-1}\,e^{-x}\,\mathrm{d}x$$

The stretched exponential function was used because it can fit non-exponential decays with a limited number of variable parameters (the β parameter describes a distribution of first-order decays when it has a value < 1), leading to a reliable and systematic approach for analysing the data. The parameters derived from fitting the fluorescence decays using Eq. (4) are given in Table 1. An estimate of Φ_{FRET} can be made using the integrated areas under the functions fitted to the fluorescence decays (deconvoluted for the IRF):[6]

$$\Phi_{FRET} = \frac{k_{FRET}}{k_R + k_{IC} + k_{ISC} + k_{FRET}} = 1 - \frac{\int_0^{\infty} I_{DA}(t)\mathrm{d}t}{\int_0^{\infty} I_D(t)\mathrm{d}t} \tag{5}$$

Table 1: Parameters for the photochrome-doped PMMA samples derived from the c-BTFO4 fluorescence decay curves.

sample	β	τ_c (ns)	τ (ns)[a]	Φ_{FRET}[b]
P1 (chloroform)			0.23[c]	
P1 PMMA			2.81[c]	
P1+P2 PMMA	0.40	0.07	0.23[c]	0.92[c]
	0.75	1.69	2.01[d]	0.28[d]
P1+P3 PMMA	0.70	1.03	1.30[c]	0.54[c]
	0.80	1.96	2.22[d]	0.21[d]

[a] error ±0.05 ns

[b] error ±0.05

[c] after UV irradiation

[d] after UV then green-light irradiation

S5. Estimation of the Förster Distance.

The Förster distance (R_0) can be calculated using the parameters that dictate the FRET efficiency for a donor-acceptor pair: the donor's fluorescence quantum yield (Φ_R), the degree of overlap between the donor's emission and acceptor's absorption spectra, i.e., overlap integral (J), the relative alignment of the donor and acceptor's transition dipole moments, i.e., orientation factor (κ^2), and refractive index of the host medium (n):[6]

$$R_0 = 0.0211 \times (n^{-4} \Phi_R \, J \, \kappa^2)^{1/6} \tag{6}$$

The overlap integral (J) is calculated by:

$$J = \int_0^\infty F_D(\lambda) \, \varepsilon_A(\lambda) \, \lambda^4 \mathrm{d}\lambda$$

where λ is the wavelength of light, $F_D(\lambda)$ is the intensity of the fluorescence spectrum of the donor at that wavelength (when the integral of the donor's fluorescence band is normalised), and $\varepsilon_A(\lambda)$ is the molar absorption coefficient of the acceptor at that wavelength.

Calculation of the Φ_R for a chromophore's excited state can be made from the radiative lifetime (τ_R) and the τ, which accounts for relaxation via radiative and non-radiative decay:

$$\Phi_R = \frac{\tau}{\tau_R} \tag{7}$$

The τ_R is also affected by the n of the surrounding medium:

$$\frac{1}{\tau_R} = \frac{n^2}{\tau_{R\,(vac)}}$$

where $\tau_{R\,(vac)}$ is τ_R in a vacuum.

Using these equations we can calculate a Φ_R estimate for c-BTFO4 in PMMA. To do this we use the Φ_R and excited state τ measured for c-BTFO4 (0.01 and 0.06 ns, respectively) in ethyl acetate solution ($n = 1.36$) and the excited state τ measured here for c-BTFO4 (2.81 ns) in PMMA ($n = 1.49$).[7] We arrive at an estimate of $\Phi_R = 0.51$ for c-BTFO4 in PMMA. For the calculation of J the molar absorption coefficients used for c-DTE and MC are 12,000 $\mathrm{M^{-1}cm^{-1}}$ and 36,800 $\mathrm{M^{-1}cm^{-1}}$, respectively.[7,8] For κ^2 we use 0.476, recommended for randomly distributed, but static donor-acceptors.[6] The c-BTFO4+c-DTE and c-BTFO4+MC pairs are calculated to have $R_0 = 2.9$ nm and 4.0 nm, respectively.

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