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Novel push—pull butadienes derived from 1,1-diaryl-2-propyn-1-ols and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione: Synthesis, absorption spectra and solvatochromic behaviour

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1. Introduction

ABSTRACT

Butadiene dyes were synthesized by the catalytic C–C coupling of 1,1-diaryl-2-propyn-1-ols with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione. The reaction, which was promoted by the 16e⁻ (η^3 -allyl)-ruthenium(II) complex [Ru(η^3 -2-C₃H₄Me)(CO)(dppf)][SbF₆], involved the Meyer–Schuster rearrangement of the aromatic alkynol and subsequent aldol-type condensation of the resulting enal with the fluorinated β -dicarbonyl compound. The absorption spectra of the dyes, as well as their solvatochromic behaviour, were studied; the structure of (4-C₆H₄OMe)₂C=CH–CH=C(COCF₃)₂ was unambiguously confirmed by means of single-crystal X-ray diffraction.

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The synthesis of organofluorine compounds has attracted a great deal of attention in recent years as the relatively small size and high electronegativity of the fluorine atom often imparts unusual properties to organic molecules into which it is incorporated [1]. In particular, useful effects have been noted when fluorine is included in photochromic [2] and biologically active molecules [3]. α , β -Unsaturated trifluoromethyl-ketones $R^1R^2C=C(R^3)C(=O)CF_3$ are organofluorine compounds that have been widely used as building blocks in synthetic organic chemistry because of their enhanced reactivity towards nucleophiles [4]. In contrast, little is known about more extended conjugated dienone systems, *i.e.* R¹R²C=CHCH=C $(R^3)C(=O)CF_3$, mainly due to the lack of general synthetic approaches [4,5]. Taking advantage of the π -electron delocalization associated to the presence of a butadienic chain and the strong accepting properties of the trifluoroacetyl group, this type of systems could be suitable for the design of new push-pull compounds by attachment of appropriate electron-donor functionalities at the opposite end of the conjugated framework ($\mathbb{R}^1/\mathbb{R}^2$ substituents). However, despite the potential applications of the resulting chromophores [6], studies in this direction have been scarce. Thus, to the best of our knowledge, only the use of the 1-substituted-4,4-bis (trifluoroacetyl)-1,3-butadiene dyes **A** and **B** (Fig. 1) for developing light filters [7] and doped polymeric non-linear optical (NLO) materials [8], respectively, has been described to date.

Based on the ability of the 16-electron $(\eta^3-\text{allyl})$ -ruthenium(II) complex [Ru $(\eta^3-2-C_3H_4Me)(CO)(dppf)$][SbF₆] (1; dppf = 1,1'-bis (diphenylphosphino)ferrocene) [9] to promote the Meyer– Schuster rearrangement of terminal propargylic alcohols into the corresponding enals **C** [10], we recently described a straightforward and general catalytic approach to conjugated dienones **D** starting from readily available diaryl-substituted alkynols and enolizable ketones (Scheme 1) [11]. This tandem isomerization/aldol condensation process, which proceeds in a one-pot manner with complete *E*-stereoselectivity, was also operative with β -diketones allowing the high-yield preparation of a number of diene-dione derivatives **E** structurally related to dyes **A**–**B** [11].

Pursuing our studies aimed at exploiting the utility of this synthetic route, this paper concerns the preparation of a series of push—pull 1,1-diaryl-4,4-bis(trifluoroacetyl)-1,3-butadiene dyes, such as **F** in Fig. 2, by catalytic C–C coupling of 1,1-diaryl-2-propyn-1-ols

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Fig. 1. Structure of bis(trifluoroacetyl)-1,3-butadiene dyes A and B.

with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione. The absorption spectral properties of these compounds, as well as their sol-vatochromic behaviour, are also discussed.

2. Results and discussion

2.1. Synthesis and characterization of the novel butadiene dyes

As shown in Scheme 2, using the experimental conditions optimized in our previous work (i.e. [alkynol]:[diketone]:[TFA]:[Ru] ratio = 20:200:2:1; 75 °C; sealed tube; solvent-free conditions) [11], a variety of 1,1-diaryl-4,4-bis(trifluoroacetyl)-1,3-butadienes (4a-f) could be synthesized in excellent yields (84–98%) starting from the readily accessible aromatic propargylic alcohols **2a-f** and commercially available 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (3). A remarkable influence of the electronic properties of the aryl rings on the reaction rates was observed. Thus, alkynols bearing electron-donating substituents **2d-f** showed less reactivity (9–11 h) as compared to the unsubstituted one 2a (3 h) [11] or those with electron-withdrawing functionalities 2b-c (30 min-2 h). As inferred by monitoring the catalytic reactions by GC, the aldol condensation between the initially formed enal and the perfluorinated β diketone is in all cases the rate limiting step of this tandem process, being favoured with electron-deficient substrates.

Following the same approach, butadiene-diones **4g** and **4h** were also selectively synthesized (83–86% yield) by reacting **3** with the



Fig. 2. Representative examples of the butadiene dyes synthesized in this work.

terminal propargylic alcohols 9-ethynyl-9-fluorenol (**2g**) and 5-ethynyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (**2h**), respectively (Scheme 3).

Characterization of compounds **4a-h** was achieved by means of standard spectroscopic techniques (GC/MS, IR as well as ¹H, ¹³C{¹H} and ¹⁹F{¹H} NMR) and elemental analyses, all data being fully consistent with the proposed formulations (details are given in the Experimental section). Moreover, the structure of **4e** could be unambiguously confirmed by means of a single-crystal X-ray diffraction analysis. An ORTEP-type drawing of the molecule, along with selected structural parameters, is shown in Fig. 3. In accord with the electronic delocalization present in the molecule, the lengths of the C(5)–C(6) (1.375(4) Å) and C(7)–C(8) (1.380(4) Å) carbon–carbon double bonds, and the single C(6)–C(7) one (1.417 (4) Å), are respectively longer and shorter than their analogous in the parent unsubstituted 1,3-butadiene molecule (C=C = 1.341 Å and C–C = 1.463 Å) [12].

The related compound **6a** could also be synthesized in high yield (94%) starting from 1,1-diphenyl-2-propyn-1-ol (**2a**) and the commercially available unsymmetric ketone 1,1,1-trifluoro-3-phenyl-2-propanone **5** (Scheme 4), thus confirming the suitability of this catalytic transformation for the construction of conjugated trifluoroacetyl-butadiene frameworks. In accord with our previous results, the reaction proceeded in a stereoselective manner with the thermodynamically more stable *E* isomer being exclusively formed [11]. In this sense, the stereochemistry of the C=C double bond in **6a** was elucidated by measuring the ³*J*_{CH} coupling constant



Scheme 1. Ru-catalyzed synthesis of conjugated dienones and diene-diones starting from diaryl-substituted alkynols and enolizable ketones.



Scheme 2. Catalytic synthesis of butadiene dyes 4a-f starting from propargylic alcohols 2a-f and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione 3.

 $(^{1}H-C=C-^{13}C)$ associated to the carbonyl carbon of the trifluoroacetyl unit, whose value (6.7 Hz) confirmed a mutually *cis* arrangement between the hydrogen atom and the C(=O)CF₃ group [13].

2.2. Absorption spectra properties

Similarly to other push–pull-type butadienes [6i,j], compounds **4a-h** and **6a** are coloured materials in the solid state (from yellow to violet) that display an intense absorption band in the visible region of their electronic absorption spectra (the absorption maxima and molar extinction coefficients measured in dichloromethane solutions are collected in Table 1). Replacement of one trifluoroacetyl unit in **4a** (entry 1) by a phenyl group (compound **6a**; entry 9) results in a slight hypsochromic shift ($\Delta\lambda_{max} = -17$ nm), pointing out the influence that the number of electron-acceptor trifluoroacetyl residues exerts in the optical properties of these new dyes.

As far as the effect of the *para*-substituents in compounds **4a-f** is concerned (entries 1–6), a bathochromic shift of the absorption band is observed when electron-donating groups are present (Fig. 4), existing a good linear correlation (r = 0.9554) between Hammett coefficients [14] and λ_{max} values (Fig. 5). Thus, in complete accord with the valence-bond resonance approach (Fig. 6), the dipolar excited state in these push–pull dyes is stabilized when X is an electron-donor substituent.

2.3. Solvatochromic behaviour

The solvatochromic properties of these new push-pull butadiene dyes were evaluated using compounds **4e** and **4f**, absorbing in the longest wavelength region, as models. To this end, UV–Vis spectra were recorded in 23 solvents having different polarities. Although individual bands in the spectra are usually overlapped (see, for example, the absorption spectrum of **4f** depicted in Fig. 4), they could be resolved [15] after applying a smoothing spline algorithm to the observed data followed by a derivative spectroscopy numerical method (only the negative peaks of the second derivatives of the smoothed spectra were used for the estimation of the position of the bands). As shown in Table 2, for both compounds, the absorption maxima undergo a large red (bathochromic) shift with increasing solvent polarity, *i.e.* $\Delta \lambda_{max} \approx 42 \text{ nm}$ for compound **4e** on going from *n*-hexane to *N*,*N*-dimethylformamide and ≈ 55 nm for compound **4f** on going from *n*-hexane to dimethyl sulfoxide. This bathochromic shift of the absorption band, which corresponds with a $\pi \rightarrow \pi^*$ electronic spectral transition (see theoretical calculations below) [16] and it is clearly visible to the naked eye (see Fig. 7), is related to a greater stabilization of the excited state relative to the ground state with increasing polarity of the solvent.

Different empirical scales (single and multiparametric) of solvent polarity have been established in order to quantify, in a simple way, solvatochromic effects [17]. In this sense, the linear correlation between the solvatochromism of dyes **4e-f** and the most commonly used solvent polarity scales was investigated (hypsochromic scales were excluded in this study). The highest linear correlation was obtained for the π^* scale, introduced by Kamlet and co-workers [18] and based on the averaged spectral behaviour of seven nitroaromatic compounds (the adopted mathematical model was $\lambda_{\text{max}} = \lambda_0 + s\pi^*$ [20]; Table 3 and Fig. 8 show the results of the least-squares procedure applied to find the best λ_0 and *s* values). The linear correlation coefficient *r* values obtained (0.9552 (**4e**) and 0.9659 (**4f**)) clearly indicate the potential utility of these butadiene dyes as new solvent polarity indicators [21].



Scheme 3. Synthesis of butadiene dyes 4g-h



Fig. 3. ORTEP-type view of the structure of **4e** showing the crystallographic labeling scheme. Thermal ellipsoids are drawn at the 10% probability level. Selected bond distances (Å) and angles (°): C(1)-C(2) = 1.540(5); C(2)-O(2) = 1.206(4); C(2)-C(5) = 1.454(4); C(3)-C(4) = 1.559(5); C(4)-O(1) = 1.206(4); C(4)-C(5) = 1.465(4); C(5)-C(6) = 1.375(4); C(6)-C(7) = 1.417(4); C(7)-C(8) = 1.380(4); C(8)-C(9) = 1.480(4); C(1)-C(2)-O(2) = 115.5(3); C(1)-C(2)-C(5) = 120.4(3); C(3)-C(4)-O(1) = 115.3(3); C(3)-C(4)-C(5) = 120.2(3); C(2)-C(5)-C(4) = 117.0(3); C(2)-C(5)-C(6) = 122.2(3); C(4)-C(5)-C(6) = 120.8(3); C(5)-C(6)-C(7) = 129.2(3); C(6)-C(7)-C(8) = 122.6(3); C(7)-C(8)-C(16) = 119.9(3); C(9)-C(8)-C(16) = 118.3(2).

2.4. Quantum chemical calculations

The electronic structure of these new dyes was further examined by theoretical models implanted in the Gaussian 03 program [22]. In particular, density functional theory (DFT) calculations (B3LYP/6-31G) were carried out to obtain information about the energy and electron distribution in the frontier MOs of **4e** (see Fig. 9). As expected, calculations clearly revealed that HOMO–LUMO excitation moves the electron distribution from the aromatic part of the molecule to the acceptor bis(trifluoroacetyl) moiety, the calculated energy gap (3.11 eV) being in good agreement with the UV/Vis data experimentally obtained for this compound. The redistribution of the electron density during the HOMO–LUMO electron transition determines the influence on the colour properties of these butadiene dyes of factors such as the effect of the substituents on the aromatic rings, or the interaction with solvents (solvatochromic behaviour).

3. Conclusions

In summary, a new series of push–pull butadiene dyes, *i.e.* $(4-C_6H_4X)_2C=CH-CH=C(COCF_3)_2$, has been synthesized by catalytic



4. Experimental

4.1. General

The manipulations were performed under an atmosphere of dry nitrogen. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and were used without further purification with the exception of the complex $[Ru(\eta^3-2-C_3H_4Me)(CO)(dppf)]$ [SbF₆] (1) [9a] and propargylic alcohols **2b** [2c], **2c** [23], **2d** [24], **2e** [23], **2f** [25] and **2h** [26], which were prepared using the methods reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. Elemental C, H and N analyses were carried out with a Perkin–Elmer 2400 microanalyzer. UV–Vis spectra were recorded on Perkin–Elmer Lambda 20 spectrometer. GC/MS measurements were performed on an Agilent 6890N equipment coupled to a 5973 mass detector (70 eV electron impact ionization) using an HP-1 MS column. NMR spectra were recorded on a Bruker DPX300 instrument at 300 MHz (¹H), 282.4 MHz (¹⁹F) or 75.4 MHz (¹³C) using SiMe₄ or CFCl₃ as standards. DEPT experiments have been carried out for all the compounds reported in this paper. All mathematical analysis (smoothing splines, second derivatives, linear and multilinear regressions) were performed with MATLAB R2009b.

4.2. Synthesis of compounds 4a-h

The catalyst $[Ru(\eta^3-2-C_3H_4Me)(CO)(dppf)][SbF_6]$ (1) (0.049 g, 0.05 mmol), the corresponding propargylic alcohol **2a-h** (1 mmol), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (**3**; 1.41 mL, 10 mmol) and trifluoroacetic acid (TFA) (7.4 µL, 0.1 mmol) were introduced into a sealed tube under a nitrogen atmosphere. The reaction mixture was heated at 75 °C for the indicated time (the reaction was monitored by regular sampling and analysis by GC/MS). After removal of volatiles under vacuum, the residue was purified by column chromatography (silica gel) using a mixture EtOAc/hexane (1:10) as eluent. Characterization data for compound **4a** were already included in our previous article [11].

4.2.1. 3-(3,3-Bis(4-fluorophenyl)allylidene)-1,1,1,5,5,5hexafluoro-2,4-pentanedione (**4b**)

Yellow oil; Reaction time: 30 min; Yield: 0.365 g (84%); Anal. Calcd for C₂₀H₁₀F₈O₂ (434.28 g mol⁻¹): C, 55.31; H, 2.32%. Found: C, 55.45; H, 2.28%; IR (Nujol): v/cm⁻¹ = 1570 (m, C=C), 1678 (s, C=O); ¹H NMR (CDCl₃): δ = 7.04 and 7.72 (d, ³J_{HH} = 12.2 Hz,



Scheme 4. Catalytic synthesis of 6a starting from alkynol 2a and 1,1,1-trifluoro-3-phenyl-2-propanone (5).

Table 1Light absorption properties of butadiene dyes 4a-h and 6a.^a

Entry	Compound	$\lambda_{max} (nm)$	$\varepsilon (M^{-1} cm^{-1})$
1	4a	388	25 621
2	4b	389	13 502
3	4c	390	16 238
4	4d	405	22 010
5	4e	447	30 047
6	4f	577	21 132
7	4g	412	28 953
8	4h	420	10 543
9	6a	371	29 661

^a Measured in dichloromethane.

1H each, =CH), 7.10–7.40 (m, 8H, H_{arom}); ¹³C{¹H} NMR (CDCl₃): $\delta = 115.3$ (q, ¹*J*_{CF} = 291.6 Hz, CF₃), 116.1 (q, ¹*J*_{CF} = 290.6 Hz, CF₃), 116.2 (d, ³*J*_{CF} = 9.7 Hz, CH_{arom}), 116.4 (d, ³*J*_{CF} = 9.5 Hz, CH_{arom}), 120.9 (s, =CH), 127.2 (s, =C), 131.8 (d, ²*J*_{CF} = 8.8 Hz, CH_{arom}), 133.0 (d, ²*J*_{CF} = 8.0 Hz, CH_{arom}), 136.1 and 136.2 (s, C_{arom}), 150.7 (br, =CH), 162.2 (s, =C), 163.4 (d, ¹*J*_{CF} = 63.7 Hz, CF_{arom}), 165.9 (d, ¹*J*_{CF} = 65.8 Hz, CF_{arom}), 178.7 (q, ²*J*_{CF} = 36.6 Hz, CO), 184.5 (q, ²*J*_{CF} = 38.7 Hz, CO); ¹⁹F{¹H} NMR (CDCl₃): $\delta = -111.2$ and -109.7 (m, 1F each, CF_{arom}), -78.1 and -74.1 (s, 3F each, CF₃); MS (EI 70eV): *m/z* (%) = 434 (15) [M⁺], 365 (10), 337 (20), 268 (10), 240 (30), 227 (100), 201 (15).

4.2.2. 3-(3,3-Bis(4-chlorophenyl)allylidene)-1,1,1,5,5,5-hexafluoro-2,4-pentanedione (**4c**)

Yellow oil; Reaction time: 2 h; Yield: 0.430 g (92%); Anal. Calcd for $C_{20}H_{10}F_6Cl_2O_2$ (467.19 g mol⁻¹): C, 51.42; H, 2.16%. Found: C, 51.56; H, 2.19%; IR (Nujol): $\nu/cm^{-1} = 1575$ (m, C=C), 1699 (s, C=O); ¹H NMR (CDCl_3): $\delta = 7.03$ (d, ${}^3J_{\rm HH} = 12.2$ Hz, 1H, =CH), 7.20 and 7.52 (d, ${}^3J_{\rm HH} = 8.6$ Hz, 2H each, CH_{arom}), 7.29 and 7.40 (d, ${}^3J_{\rm HH} = 8.8$ Hz, 2H each, CH_{arom}), 7.71 (dq, ${}^3J_{\rm HH} = 12.2$ Hz, ${}^5J_{\rm HF} = 1.0$ Hz, 1H, =CH); ${}^{13}C{}^{1}H$ NMR (CDCl_3): $\delta = 115.3$ and 116.1 (q, ${}^1J_{\rm CF} = 291.1$ Hz, CF₃), 121.3 (s, =CH), 129.5, 129.6, 130.8 and 132.3 (s, CH_{arom}), 129.0 (s, =C), 131.6, 137.3, 138.1 and 138.3 (s, C_{arom}), 150.1 (br, =CH), 161.5 (s, =C), 178.7 (q, ${}^2J_{\rm CF} = 36.5$ Hz, CO), 184.39 (q, ${}^2J_{\rm CF} = 39.0$ Hz, CO); ${}^{19}F{}^{1}H$ NMR (CDCl₃): $\delta = -76.2$ and -72.2 (s, 3F each, CF₃); MS (EI 70eV): m/z (%) = 466 (10) [M⁺], 431 (10), 397 (10), 369 (15), 334 (10), 299 (10), 276 (20), 259 (100), 236 (40), 202 (80).



Fig. 4. UV-Vis spectra of compounds 4a-f recorded in dichloromethane solution.



Fig. 5. λ_{max} *vs* Hammett coefficients for compounds **4a-f**.

4.2.3. 3-(3,3-Bis(4-methylphenyl)allylidene)-1,1,1,5,5,5hexafluoro-2,4-pentanedione (**4d**)

Orange oil; Reaction time: 11 h; Yield: 0.401 g (94%); Anal. Calcd for $C_{22}H_{16}F_6O_2$ (426.35 g mol⁻¹): C, 61.98; H, 3.78%. Found: C, 62.12; H, 3.85%; IR (Nujol): v/cm⁻¹ = 1550 (m, C=C), 1696 (s, C=O); ¹H NMR (CDCl₃): δ = 2.44 and 2.51 (s, 3H each, CH₃), 6.93 (d, ³J_{HH} = 11.7 Hz, 1H, =CH), 7.11–7.35 (m, 8H, CH_{arom}), 7.87 (dq, ³J_{HH} = 11.7 Hz, ⁵J_{HF} = 1.0 Hz, 1H, =CH); ¹³C{¹H} NMR (CDCl₃): δ = 21.7 and 21.8 (s, CH₃), 115.5 (q, ¹J_{CF} = 291.6 Hz, CF₃), 116.3 (q, ¹J_{CF} = 290.5 Hz, CF₃), 120.2 (s, =CH), 125.9 (s, =C), 129.6, 129.9, 130.1 and 131.3 (s, CH_{arom}), 134.5, 137.6, 141.3 and 142.6 (s, C_{arom}), 152.3 (br, =CH), 165.9 (s, =C), 178.9 (q, ²J_{CF} = 35.6 Hz, CO), 184.7 (q, ²J_{CF} = 38.7 Hz, CO); ¹⁹F{¹H} NMR (CDCl₃): δ = -76.1 and -72.1 (s, 3F each, CF₃); MS (EI 70eV): *m/z* (%) = 426 (20) [M⁺], 411 (10), 357 (10), 329 (40), 311 (10), 260 (10), 233 (40), 219 (100), 202 (15).

4.2.4. 3-(3,3-Bis(4-methoxyphenyl)allylidene)-1,1,1,5,5,5hexafluoro-2,4-pentanedione (**4e**)

Orange solid; Reaction time: 9 h; Yield: 0.449 g (98%); Anal. Calcd for $C_{22}H_{16}F_6O_4$ (458.35 g mol⁻¹): C, 57.65; H, 3.52%. Found: C, 57.72; H, 3.60%; IR (Nujol): v/cm⁻¹ = 1539 (m, C=C), 1685 (s, C=O); ¹H NMR (CDCl₃): δ = 3.87 and 3.91 (s, 3H each, OCH₃), 6.92 and 7.01 (d, ³*J*_{HH} = 8.8 Hz, 2H each, CH_{arom}), 7.05 (d, ³*J*_{HH} = 12.2 Hz, 1H, = CH), 7.20 and 7.35 (d, ³*J*_{HH} = 8.8 Hz, 2H each, CH_{arom}), 7.05 (d, ³*J*_{HH} = 12.2 Hz, 1H, = CH), 7.20 and 55.8 (s, OCH₃), 114.3, 114.6, 132.1 and 133.2 (s, CH_{arom}), 115.5 (q, ¹*J*_{CF} = 291.9 Hz, CF₃), 116.4 (q, ¹*J*_{CF} = 291.1 Hz, CF₃), 119.2 (s, =CH), 124.6 (s, =C), 129.7, 132.9, 162.1 and 162.9 (s, C_{arom}), 152.9 (br, =CH), 165.8 (s, =C), 178.7 (q, ²*J*_{CF} = 35.7 Hz, CO), 184.9 (q, ²*J*_{CF} = 38.1 Hz, CO); ¹⁹F{¹H} NMR (CDCl₃): δ = -76.0 and -71.9 (s, 3F each, CF₃); MS (EI 70eV): *m/z* (%) = 458 (30) [M⁺], 389 (20), 361 (60), 264 (40), 251 (100), 226 (10), 206 (10).

4.2.5. 3-(3,3-Bis(4-(dimethylamino)phenyl)allylidene)-1, 1,1,5,5,5-hexafluoro-2,4-pentanedione (**4f**)

Violet solid; Reaction time: 11 h; Yield: 0.451 g (93%); Anal. Calcd for $C_{24}H_{22}F_6N_2O_2$ (484.43 g mol⁻¹): C, 59.50; H, 4.52; N, 5.78%. Found: C, 59.63; H, 4.48; N, 5.85%; IR (Nujol): $\nu/cm^{-1} = 1517$ (m, C=C), 1597 (s, C=O); ¹H NMR (CDCl₃): $\delta = 3.10$ and 3.11 (s, 6H each, CH₃), 6.67–6.76 (m, 3H, CH_{arom}), 7.03 (d, ³J_{HH} = 12.2 Hz, 1H, = CH), 7.20–7.34 (m, 3H, CH_{arom}), 7.76–7.85 (m, 2H, CH_{arom}), 8.17 (dq, ³J_{HH} = 12.2 Hz, ⁵J_{HF} = 1.0 Hz, 1H, =CH); ¹³C{¹H} NMR (CDCl₃): $\delta = 40.2$ and 40.3 (s, CH₃), 111.3, 111.6, 133.4 and 134.3 (s, C_{arom}), 115.0 and 116.0 (q, ¹J_{CF} = 291.5 Hz, CF₃), 117.2 (s, =CH), 119.1 (s, =C), 130.9, 132.9, 152.6 and 153.2 (s, C_{arom}), 155.1 (br, =CH), 170.4 (s, =C), 173.0 (q, ²J_{CF} = 34.5 Hz, CO), 176.5 (q, ²J_{CF} = 35.5 Hz, CO); ¹⁹F{¹H} NMR (CDCl₃): $\delta = -75.2$ and -74.9 (s, 3F each, CF₃); MS (EI 70 eV): m/z (%) = 484 (100) [M⁺], 465 (5), 440 (20), 415 (5), 387 (10), 364 (50), 294 (15), 238 (20), 202 (10).



Fig. 6. The electronic conjugation in dyes 4a-f.

Table 2	
λ_{max} (nm) values of dves 4e and 4f in	various solvents and π^* values of solvents ^a

Solvent	Compound 4e	Compound 4f	π^*
n-Hexane	420	531	-0.11
Carbon tetrachloride	431	543	0.21
Diethyl ether	436	553	0.24
Ethyl acetate	442	566	0.45
1-Butanol	440	570	0.47
2-Propanol	441	570	0.48
1,4-Dioxane	440	562	0.49
Toluene	445	563	0.49
Ethanol	b	570	0.54
Benzene	446	565	0.55
Tetrahydrofuran	448	570	0.55
Methanol	b	569	0.60
2-Butanone	449	573	0.60
Acetone	447	573	0.62
Acetonitrile	448	573	0.66
Chlorobenzene	453	574	0.68
Chloroform	443	571	0.69
Dichloromethane	447	577	0.73
Nitrobenzene	462	586	0.86
Pyridine	461	583	0.87
N,N—Dimethylformamide	462	581	0.88
Benzonitrile	459	583	0.88
Dimethyl sulfoxide	^b	586	1.00

^a Spectra recorded using 6×10^{-5} M solutions. π^* values taken from reference [17] with the exception of those of benzonitrile and 2-butanone which were obtained from reference [19].

^b A broad absorption band was observed avoiding accurate λ_{max} determination.



Fig. 7. Photograph showing the colour change of dye 4f when dissolved in solvents with different polarity.

Table 3 Fitting results.^a

i itting i countor			
Compound	λο	S	r
4e	423.23 (3.80)	40.34 (6.19)	0.9552
4f	539.62 (3.90)	50.69 (6.17)	0.9659

^a Values in parentheses represent the 95% confidence limits.

4.2.6. 3-(2-Fluoren-9-ylidene-ethylidene)-1,1,1,5,5,5-hexafluoro-2,4-pentanedione (**4g**)

Orange solid; Reaction time: 5 h; Yield: 0.329 g (83%); Anal. Calcd for $C_{20}H_{10}F_6O_2$ (396.28 g mol⁻¹): C, 60.62; H, 2.54%. Found: C, 60.74; H, 2.61%; IR (Nujol): $\nu/cm^{-1} = 1544$ (m, C=C), 1690 (s, C=O); ¹H NMR (CDCl₃): $\delta = 7.21$ (d, ³*J*_{HH} = 12.7 Hz, 1H, =CH); 7.27–7.36 (m, 2H, CH_{arom}), 7.41–7.48 (m, 2H, CH_{arom}), 7.58–7.66 (m, 3H, CH_{arom}), 7.78 (d, ³*J*_{HH} = 7.8 Hz, 1H, CH_{arom}), 8.81 (dq, ³*J*_{HH} = 12.7 Hz, ⁵*J*_{HF} = 1.0 Hz, 1H, =CH); ¹³C{¹H} NMR (CDCl₃): $\delta = 115.2$ and 116.3 (q, ¹*J*_{CF} = 291.1 Hz, CF₃), 117.0 (s, =CH), 120.7, 121.2, 123.1, 126.9, 128.5, 128.6, 132.3 and 132.5 (s, CH_{arom}), 129.0 (s, =C), 135.7, 138.2, 141.6 and 143.5 (s, C_{arom}), 146.8 (br, =CH), 153.8 (s, =C), 178.6 (q, ²*J*_{CF} = 36.5 Hz, CO), 184.2 (q, ²*J*_{CF} = 39.0 Hz, CO); ¹⁹F{¹H} NMR (CDCl₃): $\delta = -76.3$ and -71.7 (s, 3F each, CF₃); MS (EI 70eV): *m/z* (%) = 396 (70) [M⁺], 376 (10), 327 (30), 299 (10), 257 (60), 229 (10), 202 (100), 186 (10).

4.2.7. 3-(2-Dibenzo[a,d]cyclohepten-5-ylidene-ethylidene)-

1,1,1,5,5,5-hexafluoro-2,4-pentanedione (4h)

Orange solid; Reaction time: 1.5 h; Yield: 0.405 g (96%); Anal. Calcd for $C_{22}H_{12}F_6O_2$ (422.32 g mol⁻¹): C, 62.57; H, 2.86%. Found: C, 62.41; H, 2.95%; IR (Nujol): v/cm⁻¹ = 1579 (m, C=C), 1699 (s, C=O); ¹H NMR (CDCl₃): $\delta = 6.64$ (d, ³*J*_{HH} = 12.0 Hz, 1H, =CH); 6.99 (br, 2H, CH=CH), 7.31 (d, ³*J*_{HH} = 7.1 Hz, 1H, CH_{arom}), 7.40–7.56 (m, 7H, CH_{arom}), 7.72 (d, ³*J*_{HH} = 12.0 Hz, 1H, =CH); ¹³C{¹H} NMR (CDCl₃): $\delta = 115.3$ and 116.1 (q, ¹*J*_{CF} = 291.1 Hz, CF₃), 126.3 (s, =CH), 127.2, 128.5, 129.3, 129.4, 129.5, 129.8, 130.1, 130.4, 131.2 and 131.6 (s, CH_{arom} and CH=CH), 127.5 (s, =C), 133.8, 134.0, 135.0 and 139.5 (s, C_{arom}), 150.5 (br, =CH), 163.8 (s, =C), 178.8 (q, ²*J*_{CF} = 36.5 Hz, CO), 184.4 (q, ²*J*_{CF} = 39.0 Hz, CO); ¹⁹F{¹H} NMR (CDCl₃): $\delta = -76.3$ and -72.2 (s, 3F each, CF₃); MS (EI 70eV): *m/z* (%) = 422 (15) [M⁺], 353 (10), 325 (50), 256 (10), 229 (50), 215 (100), 203 (10), 189 (15).



Fig. 8. λ_{max} vs π^* values for dyes **4e** and **4f** (fitting results superimposed).



Fig. 9. Surface and energy of the frontier molecular orbitals of dye 4e.

4.3. Synthesis of (*Z*)-1,1,1-trifluoro-3,6,6-triphenylhexa-3,5-dien-2-one (**6a**)

The catalyst $[Ru(\eta^3-2-C_3H_4Me)(CO)(dppf)][SbF_6]$ (1) (0.049 g, 0.05 mmol), the propargylic alcohol **2a** (0.208 g, 1 mmol), 1,1,1-trifluoro-3-phenyl-2-propanone (**5**; 1.54 mL, 10 mmol) and trifluoroacetic acid (TFA) (7.4 µL, 0.1 mmol) were introduced into a sealed tube under a nitrogen atmosphere. The reaction mixture was heated at 75 °C for 11 h (the reaction was monitored by regular sampling and analysis by GC/MS). After removal of volatiles under vacuum, the residue was purified by column chromatography (silica gel) using a mixture EtOAc/hexane (1:10) as eluent, affording **6a** as a yellow solid. Yield: 0.356 g (94%); Anal. Calcd for C₂₄H₁₇F₃O (378.39 g mol⁻¹): C, 76.18; H, 4.53%. Found: C, 76.30; H, 4.61%; IR

Table 4			
Crystal data and	structure	refinement	for 4

j	
Empirical formula	$C_{22}H_{16}F_6O_4$
Formula weight	458.35
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P21
Unit cell dimensions	
a (Å)	10.1478(6)
b (Å)	5.5480(2)
c (Å)	18.3854(11)
α (°)	90
β (°)	93.154(3)
γ (°)	90
Volume (Å ³)	1033.53(9)
Z	2
Density (calculated) (g cm ⁻³)	1.473
Absorption coefficient (mm^{-1})	0.136
F(000)	468
Crystal size (mm)	$0.35\times0.15\times0.105$
Theta range for data collection (°)	2.01-25.59
Index ranges	$-12 \le h \le 12$
·	$-6 \le k \le 6$
	$0 \leq \overline{l} \leq \overline{22}$
Reflections collected/unique	$10\ 658/3843\ [R(int) = 0.0389]$
Completeness to theta $= 25.59^{\circ}$	99.3%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3843/1/291
Goodness-of-fit on F^2	1.040
$R1^{a} [I > 2\sigma(I)]$	0.0427
$wR2^{a} [I > 2\sigma(I)]$	0.1143
R1 (all data)	0.0661
wR2 (all data)	0.1451
Largest difference peak and hole $(e \mbox{\AA}^{-3})$	0.228 and -0.260

^a $R1 = \sum |(|F_0| - |F_c|)| / \sum |F_0|; wR2 = \{\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \}^{1/2}.$

(Nujol): $\nu/cm^{-1} = 1576$ (m, C=C), 1679 (s, C=O); ¹H NMR (CDCl₃): $\delta = 6.78$ (d, ³*J*_{HH} = 11.5 Hz, 1H, =CH), 7.21–7.51 (m, 15H, CH_{arom}), 7.66 (dq, ³*J*_{HH} = 11.5 Hz, ⁵*J*_{HF} = 1.2 Hz, 1H, =CH); ¹³C{¹H} NMR (CDCl₃): $\delta = 116.1$ (q, ¹*J*_{CF} = 291.9 Hz, CF₃), 122.8 (s, =CH), 127.5, 127.6, 127.7, 127.9, 128.3, 128.7, 129.6 and 129.8 (s, CH_{arom}), 132.6 (s, =C), 134.0, 137.4 and 140.1 (s, C_{arom}), 143.6 (br, =CH), 155.0 (s, =C), 179.7 (q, ²*J*_{CF} = 33.2 Hz, CO); ¹⁹F{¹H} NMR (CDCl₃): $\delta = -70.3$ (s, 3F, CF₃); MS (EI 70eV): *m/z* (%) = 378 (60) [M⁺], 309 (60), 281 (40), 265 (50), 231 (15), 203 (100), 187 (15), 165 (20).

4.4. X-ray crystal structure determination of compound 4e

Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated solution of **4e** in dichloromethane. Data collection, crystal and refinement parameters are collected in Table 4. Diffraction data were recorded at 150(2) K on a Nonius KappaCCD single-crystal diffractometer, using Mo-K_α radiation ($\lambda = 0.71073$ Å). Images were collected at a 35 mm fixed crystaldetector distance, using the oscillation method, with 1° oscillation and 100 s exposure time per image. Data collection strategy was calculated with the program Collect [27]. Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack [28]. A semi-empirical absorption correction was applied using the program SORTAV [29].

The software package WINGX [30] was used for space group determination, structure solution and refinement. Crystal structure was solved by direct methods, using the program SIR-92 [31]. Anisotropic least-squares refinement was carried out with SHELXL-97 [32]. All non-hydrogen atoms were anisotropically refined. The hydrogen atoms were geometrically placed riding on their parent atoms with isotropic displacement parameters set to 1.2 times the U_{eq} of the atoms to which they are attached (1.5 for methyl groups). The function minimized was $[\sum w(F_0^2 - F_c^2) / \sum w(F_0^2)]^{1/2}$ where $w = 1/[\sigma^2(F_0^2) + (0.0889P)^2]$ with $\sigma^2(F_0^2)$ from counting statistics and $P = (\max(F_0^2, 0) + 2F_c^2)/3$. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography [33]. The crystallographic plots were made with PLATON [34].

5. Supplementary material

Crystallographic data for the structural analysis of compound **4e** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 758966. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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