EurJOC
European Journal of Organic Chemistry

Research Article
doi.org/10.1002/ejoc.202301136

Chemistry Europe
European Chemical Societies Publishing

www.eurjoc.org

A Novel Synthesis of Soluble, Stable Derivatives of the Perchlorinated Trityl Radical

Richard J. Bushby*[a]

A new approach to the synthesis of derivatives of the perchlorinated tritryl radical is described. It relies on the fact that, under the conditions required to fully chlorinate the *ortho* positions of a triarylmethane, there is only minimal substitution of aryl fluorine by chlorine and then on the fact that, in the mixed Cl/F substituted triarylmethanes obtained, it is possible to selectively substitute the fluorine-bearing positions using the sodium salt of n-hexanol in n-hexanol/dimethylsulfoxide. The *meta*-hexyloxy derivatives obtained are much more soluble and photostable than the parent perchlorotrityl radical. For example, the introduction of four *meta*-hexyloxy substituents gives a radical where, under white light illumination, the lifetime is improved by a factor of almost 10^4. The photostability of the radical, the lifetime of the excited state and the fluorescence all decrease as the number of *meta*-hexyloxy substituents is increased. The improvements in solubility and in photostability observed should help in creating a more diverse range of perchlorotrityl radical derivatives and in the development of new applications.

Introduction

Although solutions are not light-stable, the perchlorinated trityl radical **2**[1] is one of the most thermally stable organic radicals known. In its solid state, it is said to withstand heating in the air to 300 °C[2] and one estimate gives its half-life at room temperature as 100 years.[3] This thermal stability is attributed to the fact that, in its preferred 'propeller' conformation, the α-carbon is protected by a steric barricade of three *ortho* chlorines above and three below. However, even although the π-system is non-planar, only about half of the spin density is localised on this carbon, the rest being delocalised over the aryl rings.[4] This makes it one of the very few stable organic free radicals whose spin distribution makes it a good candidate for creating π-multi-radicals with strong co-extensive overlap of orthogonal singly occupied orbitals;[5] for creating π-multi-radicals where the high-spin state is substantially more stable than the low-spin state. As such, it should be the ideal building-block for making both high-spin non-Kekulé π-systems[6] and high-spin (ferromagnetic) polymers.[7] In terms of creating high-spin non-Kekulé π-systems a triplet ground-state perchlorinated analogue of the Schlenk hydrocarbon (two perchloro-trityl centres 1,3-linked through a shared benzene ring)[8] and a quartet ground-state triradical (three such centres 1,3,5- linked through a shared benzene ring)[9] were reported thirty years ago but attempts to create higher spin systems were not successful.[10] In more recent years there has been some additional work on polyradicals,[11] but interest has been centred more on applications of monoradical derivatives, both of the perchlorotrityl and of the closely related tris-(2,4,6-trichlorophenyl)-methyl type. These have been used to explore fundamental problems in ESR spectroscopy,[12] to explore properties of thin films of organic radicals on metal[13] and other surfaces,[1,14] as spin probes and spin labels,[15] in oximetry,[16] and in tumour imaging[16c] as well as in other sensor applications.[17] However, because of their unique optical properties, most interest has centred on the synthesis of photoluminescent derivatives for use in OLED devices.[18] All of these advances were made possible by the development of synthetic methods for introducing substituents into the perchlorotrityl nucleus; most commonly one *para*-substituent or three identical *para*-substituents.[2,18c,o,p,19] Some of the derivatives made in this way are more light-stable and more soluble than the parent chlorocarbons. For example, it has been shown that derivatives with a single *para* triphenylamine substituent are up to 75 times more light-stable than the parent system and *para* carbazole derivatives have been made[18h–j,20] where the photostability is improved by almost a factor of 10^5 (using a 355 nm laser monochromatic light source).[21] In these derivative, the improvement in photostability is attributed to intra-molecular charge-transfer[18i,j,o,22] and the improved photostability is accompanied by an increase in the quantum yield for fluorescence.[18p] However such 'charge-transfer' stabilised radicals are not generally suitable for creating high-spin systems. Such substitution almost always decreases the energy difference between the high-spin and low-spin states and sometimes it inverts the order.[23] Hence, rather than attempting to stabilise the excited state, we have attempted to shorten the lifetime of the excited state by increasing the rate of radiationless decay. For aromatic compounds, it is known that the rate of radiationless crossing from the excited state to the ground state depends, in part, on the density of CH vibrational states.[24] Hence, replacement of all of the hydrogens in a

---

[a] R. J. Bushby
School of Chemistry,
University of Leeds,
Leeds, LS2 9JT, UK
E-mail: r.j.bushby@leeds.ac.uk

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejoc.202301136

polynuclear-aromatic hydrocarbon by deuterium, removes the density of CH vibrational states and slows $S_1 \rightarrow S_0$ radiationless crossing by up to two orders of magnitude.[24b] It also normally increases the quantum yield for fluorescence.[25] Hence (it was reasoned that) the introduction of long-chain alkoxy substituents into compound **2**, the introduction of a significant density of CH vibrational states into a molecule that has none, should shorten the lifetime of the excited state(s) and so reduce both the photoreactivity and the fluorescence.

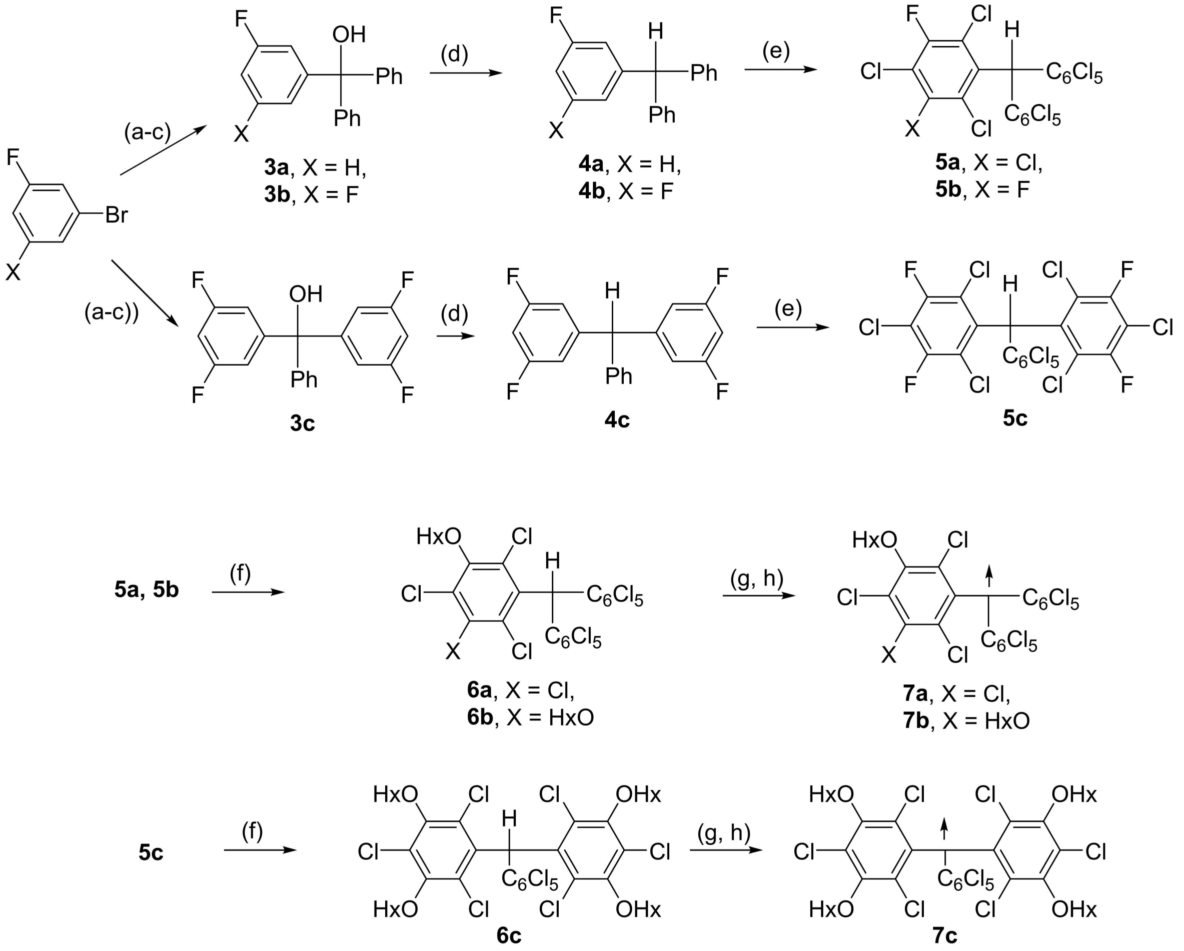
A new synthesis of perchlorotrityl radical derivatives is described and we show that, the introduction of *meta* n-hexyloxy substituents resolves the light-sensitivity problem without significantly compromising either the ground state electronic structure, the thermal-stability or the air-stability of the radicals. At the same time it gives precursors and derivatives that are much more soluble in common organic solvents; materials that (on both counts) are easier to use.

Results and Discussion

Synthesis

Pentadecachlorotriphenylmethane **1**, the precursor to the perchlorinated trityl radical **2**, can be made in several ways,[26] but the most direct method is chlorination of triphenylmethane using $SO_2Cl_2/S_2Cl_2/AlCl_3$.[26a] At the end of the reaction most of the excess SO_2Cl_2 is distilled off and, on adding water, the product precipitates as a white powder. It has very low solubility in common organic solvents. It is most soluble in chlorocarbons and is just soluble enough in $CDCl_3$ to obtain a weak ^{1}H-NMR (but not a useful ^{13}C-NMR) spectrum. The crude pentadecachlorotriphenylmethane **1** is then converted to the radical **2** by treating it with base to form the (more soluble) anion which is then oxidised; most simply NaOH/DMSO/Et_2O is followed by I_2/Et_2O.[26a] Alternatively $Bu_4N^+OH^-$ followed by chloranil is used.[27] Although the solubility of the radical is not good, it is better than that of its precursor and it can be isolated as a dilute Et_2O solution, evaporation of which gives a bright red amorphous solid which can be sublimed and which, on recrystallization, forms solvates.[28] Solutions are very sensitive to light. Under our laboratory lighting we find a half-life on the bench of about fifteen minutes. This makes column chromatography (for example) almost impossible. Under normal column chromatography conditions, the bright red band of the product becomes yellow (it photo-decomposes) as it moves down the column. Because of this sensitivity to ambient light, work on radicals in this group has sometimes been carried out using red laboratory lighting.[18l]

In making the alkoxy derivatives we aimed for a structure with substituents in the *meta* positions since these centres bear almost no spin so that substitution here should not significantly affect either the ground state electronic structure, the spin distribution or thermal/air stability of the radical.[4a] Alkoxy derivatives are unknown and we tried a number of organometallic synthetic routes (based on metallated dialkoxytrichlorobenzene)[29] without success. A triarylmethane with six *ortho* chlorines is a very sterically hindered molecule and its formation requires very forcing reaction conditions. Chlorination of a triarylmethane using $SO_2Cl_2/S_2Cl_2/AlCl_3$ works but this is a very harsh reagent and one that is only compatible with a few aromatic ring substituents. One substituent that (partly) survives these reaction conditions is aryl fluorine. Hence it is reported that, with this reagent, fluorobenzene gives a 4:1 mixture of pentachlorofluorobenzene and hexachlorobenzene. (There is only partial substitution of aryl fluorine by chlorine.)[30] In a similar manner, we found that the *meta*-flourotriphenylmethane **4a** gave a 6:1 mixture of the desired tetradecachloromonofluoro compound **5a** and the pentadecachloro compound **1**; the monofluoro compound being a ca. 3:2 mixture of compounds with the fluorine *syn* and *anti* to the α-hydrogen. The ^{1}H-NMR spectrum (in $CDCl_3$) of the crude mixture shows singlets at 6.96 and 6.94 δ for the *syn* and *anti* isomers of **5a** (unassigned) together a smaller signal at 6.99 δ due to the pentadecachlorotriphenylmethane **1** (Supporting Information). The presence of compound **1** was also confirmed by mass spectroscopy. The ^{19}F-NMR spectrum of the crude mixture shows two singlets at -105.37 and -105.52 δ. Because it is so sterically hindered, rotation of the phenyl groups is expected to be slow on the NMR timescale.[31] Neither the ^{1}H nor the ^{19}F spectra changed on raising the temperature to 60 °C and, at this temperature, a ^{1}H NOESY experiment failed to detect any magnetisation transfer. These compounds are much too insoluble to be separated by chromatography but we can now make use of the fact that, in mixed chloro/fluoro aromatics, it is possible to achieve a selective nucleophilic substitution of the aryl fluorines.[32] Hence, treatment of this mixture of **1** and **5a** with a 1 M solution of the sodium salt of n-hexanol in n-hexanol/DMSO at 100 °C gives the desired n-hexyloxy derivative **6a** which can be separated from the (unaffected) insoluble pentadecachloro compound **1**. After chromatography, the ^{1}H-NMR spectrum ($CDCl_3$) shows this to be a ca. 4:3 mixture of isomers (presumably *syn* and *anti* but unassigned). It is converted to the radical **7a** (a single isomer) using $Bu_4N^+OH^-$ followed by chloranil. A more satisfactory process starts with chlorination of 3, 5-difluorotripenylmethane **4b**. In this case there are no issues of *syn* and *anti* isomers. Furthermore, in the crude product, we could only detect ca. 5% of **5a** isomers (the products of electrophilic substitution of aryl fluorine by chlorine by the $SO_2Cl_2/S_2Cl_2/AlCl_3$ mixture). Aryl fluorine deactivates the benzene ring to electrophilic attack in the *meta* position and so these two fluorines 'mutually protect each other'. In this case the ^{1}H-NMR spectrum shows just one singlet at 6.92 δ and the ^{19}F-NMR two equal singlets for the *syn* and *anti* fluorines. This was converted to the bis-n-hexyloxytriaryl methane and thence to the trityl radical as before. In this bis-n-hexyloxy series the products are highly crystalline. Both the triaryl methane and the radical crystallise on the sides of the collection tubes during column chromatography and both are easy to recrystallize from ethanol. Unlike the parent system, recrystallization does not give a solvate. In a similar manner, the tetrafluorocompound **4c** was converted through to the tetrahexadecyl radical **7c**. In this case both **6c** and **7c** were obtained as oils (Scheme 1).



Scheme 1. Synthesis of the n-hexyloxy-substituted radicals Reagents (a) Mg/Et$_2$O/35 °C (b) PhCOPh or PhCO$_2$Me/Et$_2$O/35 °C/3 hr/63–93 % (c) H$^+$ (d) Me$_2$SiCl$_2$/NaI/DCM/acetone/0 °C/10 min/75–95 % (e) SO$_2$Cl$_2$/AlCl$_3$/S$_2$Cl$_2$/69 °C/5 hr/88–100 % (f) 1 M n-HxONa/n-HxOH/DMSO/100 °C/4–6 hr/22–62 %. Either (g) NaOH/Et$_2$O/DMSO/R.T./2 days (h) I$_2$/R.T./2 days or (g) Bu$_4$N$^+$OH$^-$/THF/DMSO/R.T./3 hr. (h) chloranil/THF/DMSO/R.T./1$^1/_2$ hr/58–79 %.

Solubility and thermal stability

As expected, the n-hexyloxy-derivatives are much more soluble in most (hydrocarbon, ether and chlorocarbon) organic solvents than the parent compounds. The solubilities of the tetra-n-hexyloxy compounds **6c** and **7c** (at room temperature) were measured in three solvents and compared to those for the parent compounds **1** and **2** (Table 1). Solubilities for the triarylmethanes **1** and **6c** were determined by the weight obtained after evaporation of aliquots of a saturated solution and those of the radicals **2** and **7c** by measurement of the UV/visible spectra (following appropriate dilution). In each case the figures quoted are an average of five measurements. As shown, the parent compounds **1** and **2** have low or very low solubility with the radical **2** being a little more soluble than its hydrocarbon precursor **1**. Solubility is highest in chlorocarbon solvents and lowest in hydrogen-boding (alcoholic) solvents. The introduction of four n-hexyloxy substituents gives materials that are infinitely miscible with hydrocarbon and chlorocarbon solvents. The solubility in ethanol remains poor.

Although thermal and air stability of radicals is key to their use there is surprisingly little quantitative information on radicals

Table 1. Solubility (g/100 mL) measured at room temperature.

	Melting point	Solubility in hexane	Solubility in dichloromethane	Solubility in ethanol
Compound **1**	320 °C (dec.)[33]	0.038 ± 0.001 g	0.36 ± 0.03 g	< 0.002 g
Radical **2**	> 300 °C (dec.)[28]	0.42 ± 0.04 g	1.8 ± 0.1 g	0.13 ± 0.02 g
Compound **6c**	oil	∞[a]	∞[a]	0.26 ± 0.03 g
Radical **7c**	oil	∞[a]	∞[a]	1.21 ± 0.06 g

[a] Fully miscible over the entire composition range.

in this series.[3,18h,j] At a qualitative level, all of the n-hexyloxy-substituted radicals we have made show excellent thermal and air stability. As with the parent radical **2**,[3,33] dilute solutions of the radicals **7a**, **7b** and **7c**, stored for a year or more at room temperature (in the dark but in contact with the air) showed no significant change to the uv/visible spectrum. In an attempt to quantify the limits of this stability, stirred dilute solutions of the radicals, in mineral oil were heated (in contact with the air) and their decomposition monitored by uv/visible spectroscopy. However, because the 'base line' drifted upwards, it was difficult to obtain meaningful kinetic data. For radical **2** it was found that, up to ca 130 °C decomposition was extremely slow but that, above this temperature, the rate increased steeply such that, by 170 °C, the approximate 'half-life' was only about 20 min. This form of temperature dependence suggests that the decomposition involves an initiated chain process. The behaviour of solutions of the tetra-n-hexyloxyradical **7c** was very similar. The onset of the decomposition process was at a slightly lower temperature (ca 120 °C). Beyond this limit the rate of decomposition began to increase quite sharply. However, it is clear that the introduction of the n-hexyloxy substituents only has a marginal effect on the thermal and air stability of the radicals. A repeat experiment in which stirred solutions of both radicals were heated at 170 °C under a nitrogen atmosphere showed almost no decomposition over several hours in the case of radical **2** and a 'half-life' of about 3 hours in case of radical **7c**.

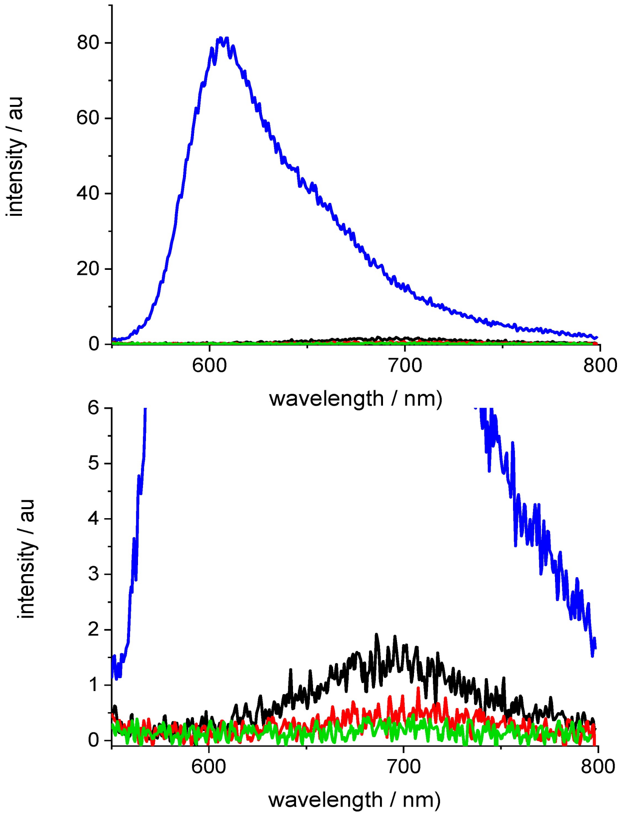


Figure 1. Fluorescence of solutions of the radicals **2** (blue), **7a** (black), **7b** (red), **7c** (green). Continuous excitation at 529 nm of $CHCl_3$ solutions (2.0 mg in 100 cc).

UV/visible spectra, fluorescence and photostability

The uv/visible spectra of the n-hexyloxy-substituted radicals **7a**–**7c** only show small differences to that of the parent radical **2**. (Data tabulated in the Supporting Information) The biggest difference is in the wavelengths of the longest wavelength absorption peaks (in $CHCl_3$ 509 and 564 nm for **2** and 518 and 569 nm for **7b**). Compared to a related system in which there is significant charge-transfer in the excited state[22] the effect of solvent polarity on the uv/visible spectra is weak. Hence in the case of the radical **7b**, the main adsorption maximum occurs at 382.6 nm in hexane, ethanol, diethyl ether and acetone, 382.9 nm in acetonitrile, 384.4 nm in dichloromethane and 386.6 nm in benzene (Supporting Information). However, although the uv/vis spectra are little affected by n-hexyloxy substitution this is not the case for the fluorescence spectra. Previous studies of the fluorescence of **2** have shown that it gives a weak emission (quantum efficiency 0.015 in hexane) at 606 nm.[34] Figure 1 shows a comparison of the fluorescence emission spectra for **2** and **7a**–**7c**. In each case a solution of 2 mg of the radical in 100 mL of $CHCl_3$ was used and the same (continuous irradiation) excitation conditions. As expected, for radical **2**, the fluorescence maximum, is at ca. 606 nm. However, the mono-n-hexyloxy radical **7a** shows only a very weak emission at ca 690 nm, the di-n-hexyloxy radical **7b** an even weaker emission and that for the tetra-n-hexyloxy radical **7c** is barely detectable. The main component of the decay of the fluorescence of **2** is associated with a half-life of 16.9 ns, that of **7a** with a half-life of 0.85 ns and that of **7b** with a half-life of 0.58 ns[17–18] decreases in the lifetime of the excited states that reflect the decrease in the fluorescence yield. (Supporting Information)

The photochemistry of the radical **2** is complex.[34–35] The ratio of products obtained depends on the solvent and whether an oxygen-free atmosphere is used. However, the dominant reaction involves elimination of two chlorines and formation of a fluorenyl derivative. Whereas it proved difficult to obtain reproducible kinetic data from the thermal decomposition of these radicals using uv/visible spectroscopy (because of base-line drift) this was not a significant problem with the photodecomposition so that it was possible to obtain reproducible first order kinetics by following the disappearance of the intense, narrow peak at ca. 384 nm in the uv/visible spectrum. In the case of radical **2** this yielded a half-life of about 15 min when the solution was left exposed to the light on the laboratory bench. In the case of the tetra-n-hexyloxy radical **7c**, under the same conditions, the half-life was over a month. However, over this period, there were cycles of night and day so that the level of illumination was not constant. Unfortunately, most of previous quantitative studies of the photostability of related radicals has used monochromatic laser light[18g,j,k,m,n,p] making it difficult to relate to normal white light laboratory conditions. To try to obtain a more meaningful comparison (as well as faster reaction rates) an apparatus was built in which the solution of the radical was held a fixed distance from an intense LED white-light source. The system used is shown in the Supporting Information. The kinetic data obtained is shown in Figure 2 and the numerical data is displayed in Table 2. As may be seen, the introduction of *meta* fluorines into the system has only a small effect on the decomposition rate. However, the introduction of the n-hexyloxy substituents has a dramatic effect and, as with the fluorescence data, the more n-hexyloxy substituents there are, the more the density of CH vibrational states is increased, the more that radiationless crossing from the excited state surface to the ground state surface is favoured, the more photostable the radicals become. As in the case of the fluorescence data (Figure 1), the biggest effect is seen when a single n-hexyloxy group is introduced (the rate decreases by a factor of almost a thousand). The photostability is improved by another factor of ten when there are two n-hexyloxy groups, but the effect seems to saturate out, such that there is only a small further increase in photostability when there are four n-hexyloxy groups. Overall, for **7c** relative to the parent radical **2**, the lifetime of the solutions under white light illumination is improved by a factor of about 10^4.[4a]

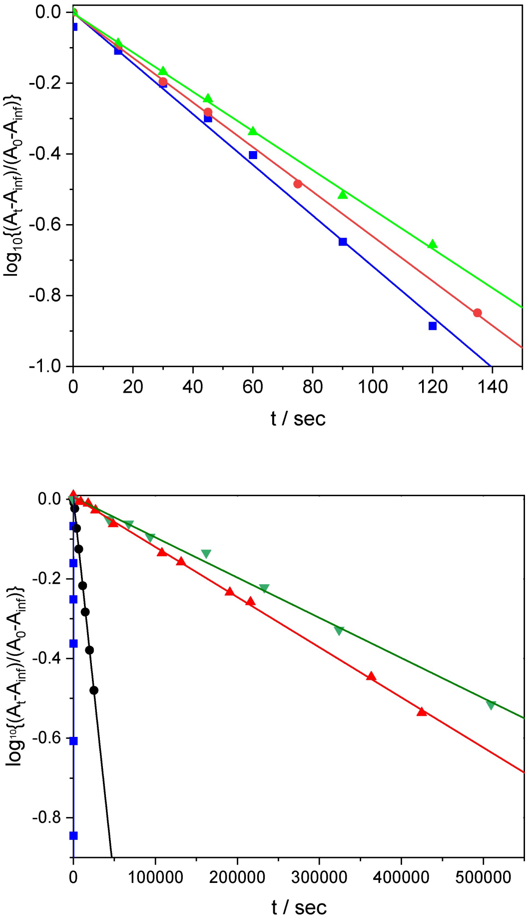


Figure 2. Photokinetic studies; Dichloromethane solutions with the LED light source. (above) comparison of the rates of photodecomposition for the radicals **2** (parent system, blue), **8a** (monofluoro, red) and **8b** (difluoro, green). (below) Comparison of the rates of photodecomposition for the radicals **2** (parent system, blue), **7a** (mono-n-hexyloxy, black), **7b** (di-n-hexyloxy, red) and **7c** (tetra-n-hexyloxy, green)

EPR and NMR spectra

EPR spectra were measured in dilute dichloromethane solution at 200 K and are shown in the Supporting Information. Comparison of the extracted parameters shows that, in terms of the measured g-values, there are no significant differences between the parent radical **2** and the fluorinated radicals **8a** and **8b** or the hexyloxy substitituted radicals **7a** and **7b**. Similarly the measured ^{13}C hyperfine splittings are almost the same throughout. The biggest difference between values for the α-C is that between the difluorinated radical (a = 85 MHz) and the mono hexyloxy radical (a = 83.5 MHz). This shows that, *meta* substitution with either fluorine or hexyloxy does not significantly change the spin distribution either as between the central carbon and the aryl rings or as between the substituted and unsubstituted aryl rings.

As previously noted, the precursor **1** to the perchlorinated trityl radical is just soluble enough in $CDCl_3$ to obtain a weak ^{1}H-NMR spectrum. However, in the ^{13}C-NMR spectrum, only the strongest signals can be seen above the level of the noise. For the tetrakis-n-hexyloxy compounds **6a–c**, solubility is not a problem. The ^{13}C-NMR spectra obtained show 8–10 resonances assigned to the n-hexyloxy residues and 16–33 resonances associated with the aromatic rings. Many of these appear as closely spaced pairs. The number of peaks obtained shows that the 'flip-flop' motion associated with the interconversion of the

Table 2. Photodecomposition kinetics. Solutions in dichloromethane.

Radical	ν_H[a]	light source	k_1/sec^{-1}	relative rate	half life/sec (half life/days)
Parent, **2**	0	ambient	$7.28\pm0.56\times10^{-4}$	4.4×10^{-2}	9.2×10^{2}
Parent, **2**	0	LED	$1.65\pm0.06\times10^{-2}$	1.00	42
F_1,[b] **8a**	0	LED	$1.45\pm0.01\times10^{-2}$	0.87	48
F_2,[c] **8b**	0	LED	$1.27\pm0.02\times10^{-2}$	0.76	55
$(HxO)_1$, **7a**	0.25	LED	$4.44\pm0.04\times10^{-5}$	2.7×10^{-3}	1.6×10^{4} (0.19)
$(HxO)_2$, **7b**	0.36	LED	$2.90\pm0.03\times10^{-6}$	1.8×10^{-4}	2.4×10^{5} (2.8)
$(HxO)_4$, **7c**	0.52	LED	$2.41\pm0.06\times10^{-6}$	1.5×10^{-4}	2.9×10^{5} (3.4)

[a] ν_H, Fraction of hydrogen atoms; a measure of the density of CH vibrational states. [b] Contained ca. 20 % **2**. [c] Contained ca. 5 % **8a**.

right-hand and left-hand propeller conformations is slow on the NMR timescale.

Because of issues of instability and of paramagnetic broadening, it is not usual to use NMR spectroscopy to characterise organic free radicals. However, for these n-hexyloxy-substituted radicals, it is possible to obtain useful, interesting NMR spectra. When the triarylmethanes **6** are converted to the radicals **7** (because of paramagnetic broadening) the signals associated with the aromatic ring and the first carbon of the hexyloxy chain are lost. However, broadened resonances associated with the rest of the hexyloxy chain can still be observed. The ^{1}H-NMR spectrum of the radicals show five broad peaks integration ratio 1:1:4:2:3 and the proton-decoupled ^{13}C-NMR show five singlets. (Figure 3). Table 3 gives the chemical shifts for **6c** and **7c** but those for **6a**, **6b** and **6c** are almost the same as each other as are those for **7a**, **7b** and **7c** (Supporting Information).

The assignments of the NMR signals for **6c** are based on 2D NMR studies and agree with those for a number of other n-hexyloxyaryl compounds for which unambiguous assignments have been made.[36] Indeed, (except for C1 of the n-hexylyoxy chain) the ^{13}C-NMR chemical shifts for aryl n-hexyloxy chains are found to vary very little from compound to compound. The assignment of the NMR spectra of the radical **7c** is more difficult. Making use of the results of 2D-NMR studies, the signal at δ 0.89 in the ^{1}H-NMR spectrum is assigned to the methyl group and the signal at δ 1.35 to CH$_2$ groups at positions 4 and 5. Unfortunately, in the COSY, HMQC and NOESY ^{1}H/^{1}H and ^{1}H/^{13}C correlation spectra, the cross-peaks associated with the ^{1}H-NMR signals at δ 1.99, 1.85 and 1.21 are not clearly above the level of noise. This is a consequence of the very short relaxation times which reduce magnetisation transfer. However, by recording an HSQC spectrum with a shorter recycle delay and increased ^{13}C resolution, it

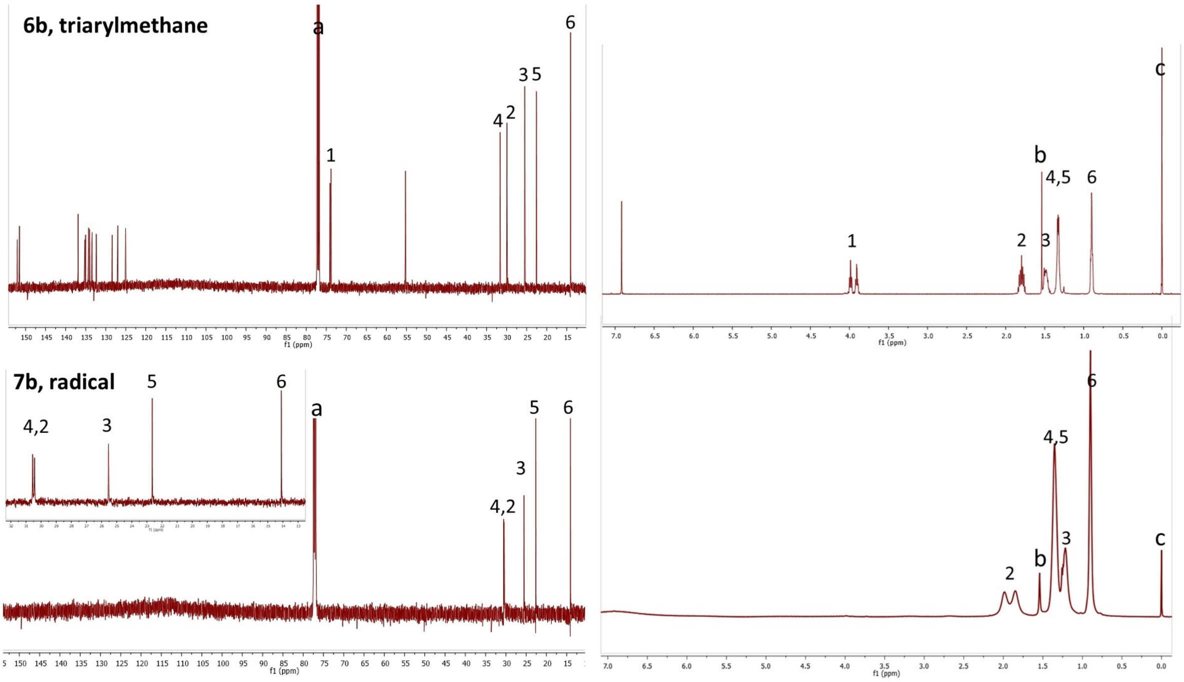


Figure 3. Comparison of the ^{13}C-NMR (10–155 δ, left) and ^{1}H-NMR (0–7 δ, right) spectra of the di-n-hexyloxytriarylmethane **6b** with that of the corresponding di-n-hexyloxy radical **7b**. The resonances associated with the n-hexyloxy chains are labelled 1–6, a = CDCl$_3$, b = H$_2$O, c = TMS. The insert in the ^{13}C-NMR of **7b** is an expansion of the ca. δ 10–35 region showing the resolution of the resonances for carbons 2 and 4 of the alkoxy chain.

Table 3. NMR data for positions 2–6 of the hexyloxy chains for compounds **6c** and **7c**; the tetrahexyloxy triarylmethane and the tetrahexyloxy radical.

	CH$_2$-2	CH$_2$-3	CH$_2$-4	CH$_2$-5	CH$_3$-6
δ ^{1}H **6c**[a]	1.80	1.49	1.34	1.34	0.89
δ ^{1}H **7c**[a]	1.99, 1.85	1.21	1.35[c]	1.35[c]	0.89
Δδ ^{1}H **6c**–**7c**[a]	−0.19. −0.05	+0.28	−0.01	−0.01	0.00
δ ^{13}C **6c**[a]	30.27	25.82	31.94	22.91, 22.92	14.38
δ ^{13}C **7c**[a]	30.61	25.84	30.84	22.91	14.37
Δδ ^{13}C **6c**–**7c**[a]	−0.34	−0.02	+1.09	0.00, −0.01	−0.01
T$_1$ ^{1}H **7c**/msec[b]	10 ± 3, 10 ± 3	16 ± 3	48 ± 3[c]	48 ± 3[c]	127 ± 4
T$_1$ ^{13}C **7c**/msec[b]	120 ± 12	178 ± 12	310 ± 28	605 ± 36	907 ± 33

[a] CDCl$_3$ solution; [b] CDCl$_3$ solution, 8.0 mg/mL, 25°C; [c] Signals not resolved.

was possible to show clear correlations between the proton at δ 1.21 and the carbon at δ 30.85 ppm and between the protons at δ 1.99 and 1.85 and the carbon at δ 30.61 (Supporting Information). Hence the signals are assigned as shown in Table 3 and in Figure 3. Measurement of the ^{1}H and ^{13}C T_1 relaxation times shows that, as expected, these decrease monotonically along the chain. The closer the atoms are to the spin-bearing aryl nucleus the shorter the relaxation time becomes (Table 3).

The feature of these spectra which is difficult to understand is why, in the ^{1}H-NMR spectra of **7a**, **7b** and **7c**, the signal for the methylene at C2 appears as *two* broad singlets. Since the spectra of all three radicals are essentially the same, this is not an issue of whether or not, within the propeller conformation, the n-hexyloxy groups are adjacent to a substituted or unsubstituted ring. Since the chemical shifts for these two resonances (in ppm for **7b** in $CDCl_3$) are the same when measured at 300 and 500 MHz the 'splitting' is not the result of a scalar coupling. Also, (for **7c** in $CDCl_3$) only minor changes were observed over the concentration range 0.4 to 40.0 mg/mL and only small differences in the chemical shifts as measured in $CDCl_3$, in d_8-dioxane and in d_6-benzene. Hence, the 'splitting' unlikely to be the result of formation of some kind of unsymmetrical complex or the result of 'non-covalent dimer' formation. Since the spectra for **7b** in $CDCl_3$ show only general changes in the linewidths for of all of the signals between −80 and +60 °C it also seems unlikely that slow chemical exchange is a significant issue. However, it is just possible that the 'splitting' results from slow interconversion of the two propeller conformations combined with an orthogonal geometry for the Ar-alkoxy bond and slow rotation about this bond. Indeed, it is known that interconversion of the propeller conformations is very slow[8,37] and a survey of all of the crystal structures in the Cambridge Structural Database in which a methoxy group is flanked by two *ortho*-chlorines yields C–C–O–Me dihedral angles in the range 75–105°. Furthermore, model 6–31G* MO calculations on 2,6-dichloromethoxybenzene, 2,3,5,6-tetrachloromethoxybenzene and 2,6-dichloroethoxybenzene (with full geometry optimization) gave C–C–O–R dihedral angles very close to 90°. However, calculations in which this dihedral angle was fixed (0–90 degrees) and the rest of the geometry optimized gave barriers for rotation about this bond of 6.1, 6.9 and 6.6 kcal mol^{-1} respectively (Supporting Information). This is a substantial barrier but it is less than half of that needed to give slow rotation on the relevant NMR timescale. Hence, the most probable explanation of the fact that, in the ^{1}H-NMR spectrum, the signal for with the second methylene of the chain appears as two singlets is that this arises because the two hydrogens in this methylene group are diasteriotopic.

Conclusions

The synthetic strategy described in this paper, perchlorination of a fluorinated triarylmethane followed by nucleophilic substitution, (for the first time) allows alkoxy substituents to be introduced into the perchlorinated trityl nucleus. Because of the ease with which *meta* substituted derivatives can be made and with which derivatives with more than one substituent can be made, and because it should be possible to use nucleophiles other than alkoxy, this approach should help in creating other perchlorotrityl radical derivatives and hence help to extend the range of applications of radicals in this group.

As expected, and, as evidenced by the EPR and uv/visible spectra, the introduction of *meta*-n-hexyloxy substituents into the perchlorotrityl nucleus has little effect on the spin distribution or the ground state electronic structure of these radicals. It also has little effect on their thermal/air stability. Crucially the steric barricade provided by the *ortho*-chlorines remains unaffected and the α-carbon is still shielded from attack. The big effect of introducing the n-hexyloxy substituents is on the solubility of the radicals and (particularly) their precursors and on their fluorescence and photostability. The lack of a significant solvatochromic effect and the fact that fluorescence is supressed in these derivatives suggest that the improved photostability arises from a different mechanism to that operating in the 'charge-transfer' stabilised derivatives developed for the OLED work. Qualitatively the improved photostability, shortened excited state lifetimes and supressed fluorescence could all be explained in terms of an increase in the rate of radiationless deactivation of the excited state related to the introduction and increase in density of CH vibrational states. However, it is difficult to ascribe an increase in lifetime of four orders of magnitude solely to such an effect.[24b,25] Regardless of the actual mechanism involved, the excellent thermal stability and air stability of these n-hexyloxy-substituted radicals combined with their improved photo-stability and solubility means that they are much easier to work with. Compared to the parent perchlorinated trityl radical, solutions of the radicals 'left exposed to the light' have a half life of months rather than of minutes. This means that operations like t.l.c., column chromatography, recrystallization etc. can be performed without having to take extraordinary measures[18l] to exclude damaging wavelengths of light and this too should help in the further development of the field.

Acknowledgements

This work was mostly self-funded but, following my retirement, thanks are due to the School of Physics and Astronomy for the provision of bench and office space and to the School of Chemistry for free access to NMR and MS facilities. Thanks also to Dr. B. Johnson for the build of the photo-stability testing apparatus, Dr. A.M. Hancock for the fluorescence lifetime measurements, J. Dickinson and Dr. A. Heyam for the VT, HSQC and T_1 NMR measurements and A. Brookfield (EPSRC UK National EPR Facility at the University of Manchester) for the EPR spectra.

Conflict of Interests

There are no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article https://doi.org/10.5518/1440.

Keywords: Polychlorination · Trityl radicals · Photostability · Stable radicals

[1] I. Ratera, J. Vidal-Gancedo, D. Maspoch, S. T. Bromley, N. Crivillers, M. Mas-Torrent, *J. Mater. Chem. C* **2021**, *9*, 10610–10623.
[2] M. Ballester, J. Riera, J. Castaner, A. Rodriguez, C. Rovira, J. Veciana, *J. Org. Chem.* **1982**, *47*, 4498–4505.
[3] M. Ballester, *Acc. Chem. Res.* **1985**, *18*, 380–387.
[4] a) G. R. Luckhurst, J. N. Ockwell, *Tetrahedron Lett.* **1968**, *9*, 4123–4126; b) I. Alcón, S. T. Bromley, *RSC Adv.* **2015**, *5*, 98593–98599.
[5] a) A. Rajca, *Chem. Rev.* **1994**, *94*, 871–893; b) W. T. Borden, E. R. Davidson, *J. Am. Chem. Soc.* **1977**, *99*, 4587–4594; c) R. J. Bushby, N. Taylor, R. A. Williams, *J. Mater. Chem.* **2007**, *17*, 955–964.
[6] a) P. M. Lathi, *Magnetic Properties of Organic Materials*, Marcel Dekker, New York, **1999**; b) C. Shu, Z. M. Yang, A. Rajca, *Chem. Rev.* **2023**, *123*, 11954–12003.
[7] a) A. A. Ovchinnikov, *Theor. Chem. Acta* **1978**, *47*, 297–304; b) A. Rajca, J. Wongsriratanakul, S. Rajca, *Science* **2001**, *294*, 1503–1505; c) R. J. Bushby, D. R. McGill, K. M. Ng, N. Taylor, *J. Mater. Chem.* **1997**, *7*, 2343–2354.
[8] J. Veciana, C. Rovira, M. I. Crespo, O. Armet, V. M. Domingo, F. Palacio, *J. Am. Chem. Soc.* **1991**, *113*, 2552–2561.
[9] J. Veciana, C. Rovira, N. Ventosa, M. I. Crespo, F. Palacio, *J. Am. Chem. Soc.* **1993**, *115*, 57–64.
[10] D. Ruiz-Molina, J. Veciana, F. Palacio, C. Rovira, *J. Org. Chem.* **1997**, *62*, 9009–9017.
[11] a) S. F. Wu, M. C. Li, H. Phan, D. G. Wang, T. S. Herng, J. Ding, Z. G. Lu, J. S. Wu, *Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 8007–8011; b) Y. Hattori, E. Michail, A. Schmiedel, M. Moos, M. Holzapfel, I. Krummenacher, H. Braunschweig, U. Muller, J. Pflaum, C. Lambert, *Chemistry* **2019**, *25*, 15463–15471.
[12] a) D. Banerjee, J. C. Paniagua, V. Mugnaini, J. Veciana, A. Feintuch, M. Pons, D. Goldfarb, *Phys. Chem. Chem. Phys.* **2011**, *13*, 18626–18637; b) J. L. Huffman, M. Poncelet, W. Moore, S. S. Eaton, G. R. Eaton, B. Driesschaert, *J. Phys. Chem. B* **2021**, *125*, 7380–7387.
[13] a) C. Simao, M. Mas-Torrent, J. Veciana, C. Rovira, *Nano Lett.* **2011**, *11*, 4382–4385; b) V. Mugnaini, A. Calzolari, R. Ovsyannikov, A. Vollmer, M. Gonidec, I. Alcon, J. Veciana, M. Pedio, *J. Phys. Chem. Lett.* **2015**, *6*, 2101–2106.
[14] C. Simao, M. Mas-Torrent, N. Crivillers, V. Lloveras, J. M. Artes, P. Gorostiza, J. Veciana, C. Rovira, *Nat. Chem.* **2011**, *3*, 359–364.
[15] M. Ballester, J. Riera, J. Castaner, C. Rovira, J. Veciana, C. Onrubia, *J. Org. Chem.* **1983**, *48*, 3716–3720.
[16] a) J. H. Wang, V. Dang, W. Zhao, D. N. Lu, B. K. Rivera, F. A. Villamena, P. G. Wang, P. Kuppusamy, *Bioorg. Med. Chem.* **2010**, *18*, 922–929; b) I. Dhimitruka, Y. A. Alzarie, C. Hemann, A. Samouilov, J. L. Zweier, *Bioorg. Med. Chem. Lett.* **2016**, *26*, 5685–5688; c) A. Bratasz, A. C. Kulkarni, P. Kuppusamy, *Biophys. J.* **2007**, *92*, 2918–2925; d) J. Z. Sostaric, R. P. Pandian, A. Bratasz, P. Kuppusamy, *J. Phys. Chem. B* **2007**, *111*, 3298–3303.
[17] Y. Hattori, S. Kimura, T. Kusamoto, H. Maeda, H. Nishihara, *Chem. Commun.* **2018**, *54*, 615–618.
[18] a) D. Mesto, Y. Dai, C. N. Dibenedetto, A. Punzi, J. Krajčovič, M. Striccoli, F. Negri, D. Blasi, *Euro. J. Org. Chem.* **2023**, *26*, e202201030; b) A. Heckmann, S. Dummler, J. Pauli, M. Margraf, J. Kohler, D. Stich, C. Lambert, I. Fischer, U. Resch-Genger, *J. Phys. Chem. C* **2009**, *113*, 20958–20966; c) A. Heckmann, C. Lambert, *J. Am. Chem. Soc.* **2007**, *129*, 5515–5527; d) A. Heckmann, C. Lambert, M. Goebel, R. Wortmann, *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 5851–5856; e) E. Cho, V. Coropceanu, J. L. Bredas, *J. Am. Chem. Soc.* **2020**, *142*, 17782–17786; f) J. Luo, X. F. Rong, Y. Y. Ye, W. Z. Li, X. Q. Wang, W. Wang, *Molecules* **2022**, *27*, 1632; g) Y. Hattori, T. Kusamoto, H. Nishihara, *RSC Adv.* **2015**, *5*, 64802–64805; h) Q. M. Peng, A. Obolda, M. Zhang, F. Li, *Angew. Chem. Int. Ed. Engl.* **2015**, *54*, 7091–7095; i) A. Obolda, X. Ai, M. Zhang, F. Li, *ACS Appl. Mater. Interfaces* **2016**, *8*, 35472–35478; j) X. Ai, Y. X. Chen, Y. T. Feng, F. Li, *Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 2869–2873; k) P. M. Burrezo, V. G. Jiménez, D. Blasi, I. Ratera, A. G. Campaña, J. Veciana, *Angew. Chem. Int. Ed. Engl.* **2019**, *58*, 16282–16288; l) P. Mayorga-Burrezo, V. G. Jimenez, D. Blasi, T. Parella, I. Ratera, A. G. Campana, J. Veciana, *Chemistry* **2020**, *26*, 3776–3781; m) C. H. Liu, E. Hamzehpoor, Y. Sakai-Otsuka, T. Jadhav, D. F. Perepichka, *Angew. Chem. Int. Ed. Engl.* **2020**, *59*, 23030–23034; n) S. Kimura, M. Uejima, W. Ota, T. Sato, S. Kusaka, R. Matsuda, H. Nishihara, T. Kusamoto, *J. Am. Chem. Soc.* **2021**, *143*, 4329–4338; o) L. Chen, M. Arnold, R. Blinder, F. Jelezko, A. J. C. Kuehne, *RSC Adv.* **2021**, *11*, 27653–27658; p) Y. Hattori, S. Tsubaki, R. Matsuoka, T. Kusamoto, H. Nishihara, K. Uchida, *Chem. Asian J.* **2021**, *16*, 2538–2544; q) M. E. Arnold, A. J. C. Kuehne, *Dyes Pigm.* **2023**, *208*, 110863.
[19] a) M. Ballester, J. Castaner, J. Riera, A. Ibanez, J. Pujadas, *J. Org. Chem.* **1982**, *47*, 259–264; b) C. Rovira, D. Ruiz-Molina, O. Elsner, J. Vidal-Gancedo, J. Bonvoisin, J. P. Launay, J. Veciana, *Chem. Eur. J.* **2001**, *7*, 240–250.
[20] Q. X. Jin, S. X. Chen, Y. T. Sang, H. Q. Guo, S. Z. Dong, J. L. Han, W. J. Chen, X. F. Yang, F. Li, P. F. Duan, *Chem. Commun.* **2019**, *55*, 6583–6586.
[21] H. Guo, Q. Peng, X. K. Chen, Q. Gu, S. Dong, E. W. Evans, A. J. Gillett, X. Ai, M. Zhang, D. Credgington, V. Coropceanu, R. H. Friend, J. L. Bredas, F. Li, *Nat. Mater.* **2019**, *18*, 977–984.
[22] M. Steeger, S. Griesbeck, A. Schmiedel, M. Holzapfel, I. Krummenacher, H. Braunschweig, C. Lambert, *Phys. Chem. Chem. Phys.* **2015**, *17*, 11848–11867.
[23] G. Allinson, R. J. Bushby, M. V. Jesudason, J. L. Paillaud, N. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1997**, 147–156.
[24] a) M. Bixon, J. Jortner, *J. Chem. Phys.* **1968**, *48*, 715–726; b) J. B. Binks, *Photophysics of Aromatic Molecules*, John Wiley and Sons, **1970**.
[25] V. L. Ermolaev, *Opt. Spectrosc.* **2016**, *121*, 567–584.
[26] a) M. Ballester, J. Riera-Figueras, J. Castaner, C. Badfa, J. M. Monso, *J. Am. Chem. Soc.* **1971**, *93*, 2215–2225; b) M. Ballester, J. Riera, J. Castaner, C. Rovira, O. Armet, *Synthesis* **1986**, 64–66.
[27] O. Armet, J. Veciana, C. Rovira, J. Riera, J. Castaner, E. Molins, J. Rius, C. Miravitlles, S. Olivella, J. Brichfeus, *J. Phys. Chem.* **1987**, *91*, 5608–5616.
[28] J. Veciana, J. Carilla, C. Miravitlles, E. Molins, *J. Chem. Soc. Chem. Commun.* **1987**, 812–814.
[29] G. A. Kraus, Y. Zeng, *Synth. Commun.* **2000**, *30*, 2133–2141.
[30] a) A. F. Andrews, C. Glidewell, J. C. Walton, *J. Chem. Res. Synop.* **1978**, *2*, 294; b) C. Glidewell, J. C. Walton, *J. Chem. Soc. Chem. Commun.* **1977**, 915–916.
[31] a) D. Gust, K. Mislow, *J. Am. Chem. Soc.* **1973**, *95*, 1535–1547; b) J. Sedo, N. Ventosa, M. A. Molins, M. Pons, C. Rovira, J. Veciana, *J. Org. Chem.* **2001**, *66*, 1567–1578.
[32] a) G. G. Yakobson, L. S. Kobrina, N. N. Vorozhts, *J. Gen. Chem. USSR* **1965**, *35*, 136; b) K. J. Kolonko, M. L. Deinzer, T. L. Miller, *Synthesis* **1981**, 133–135.
[33] M. Ballester, J. Riera, J. Castaner, C. Badia, J. M. Monso, *J. Am. Chem. Soc.* **1971**, *93*, 2215–2225.
[34] S. R. Ruberu, M. A. Fox, *J. Phys. Chem.* **1993**, *97*, 143–149.
[35] M. A. Fox, E. Gaillard, C. C. Chen, *J. Am. Chem. Soc.* **1987**, *109*, 7088–7094.
[36] a) Y. Jayasubba Reddy, V. Agarwal, A. Lesage, L. Emsley, K. V. Ramanathan, *J. Magn. Reson.* **2014**, *245*, 31–37; b) in *SDBSWeb : https://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology)*, **2023**.
[37] J. Veciana, C. Rovira, M. I. Crespo, O. Armet, V. M. Domingo, F. Palacio, *J. Am. Chem. Soc.* **1991**, *113*, 2552–2561.

Manuscript received: November 3, 2023
Revised manuscript received: January 26, 2024
Accepted manuscript online: January 29, 2024
Version of record online: February 19, 2024