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Blue two-photon excited fluorescence of several D-π-D, A-π-A, and D-π-A compounds featuring dimesitylboryl acceptor ☆

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Abstract

Several donor-π-donor (D-π-D), acceptor-π-acceptor (A-π-A), and donor-π-acceptor (D-π-A) types of organic compounds with fluorene as π bridge and dimesitylboryl group as electron acceptor, which show strong two-photon excited blue fluorescence, have been synthesized and structurally investigated. The symmetric A-π-A type of compound exhibits the shortest wavelength of two-photon excited fluorescence (TPEF) at $\lambda_{em} = 405$ nm under the excitation of $\lambda_{ex} = 730$ nm; the unsymmetric D-π-A type of compound with diphenylamino as donor exhibits the most intense TPEF at blue region ($\lambda_{em} = 484$ nm) with a two-photon absorption cross-section of 425 GM under $\lambda_{ex} = 800$ nm.

Keywords: Dimesitylboryl; Two-photon excited fluorescence; X-ray structure

1. Introduction

In recent years, there has been great research interest in organic molecules, which show strong two-photon excited fluorescence (TPEF) [1–5]. If the two-photon excitation is carried out by a tightly focused laser beam, the TPEF can be confined in a small volume of the order of λ^3. Thus, blue TPEF at short wavelength will have high spatial resolution for various photonic applications, such as three-dimensional optical data storage [2], two-photon laser scanning fluorescence microscopy [3] and microfabrication [4]. Unfortunately, most reported TPEF to date are in the green-to-red (500–700 nm) light region. New organic blue TPEF emitters are highly desirable. To our knowledge, the only known TPEF emitters around 400 nm are 4,4′-bis(di-*n*-butylamino)-*E*-stilbene (emitting at $\lambda_{em} = 410$ nm) type of D-π-D compounds [5].

In our design for blue TPEF compounds, two strategies have been considered. Firstly, fluorenyl has been adopted as a π-bridge. By comparison with the most frequently appeared stilbene π-bridge, the fluorescence of a D-fluorenyl-D compound can have at least 30 nm blue shift relative to that of its D-stilbene-D counterpart. Meanwhile, as confirmed by the two structures in this work, fluorenyl has perfect planarity and π-conjugation because of its much better rigidity in comparison with that of stilbenyl. Secondly, because of the electron-deficient nature of the B(III), trivalent organoboron group has been adopted as acceptor. In recent years, there are indeed several reports about the interesting nonlinear optical, electro-optical, and electron-transporting properties of the polymetric and molecular materials containing dimesitylboryl group, as reviewed by Marder [6].

In this paper, four typical symmetric (D-π-D and A-π-A) and asymmetric (D-π-A) compounds with fluorenyl as π-bridge and dimesitylboryl as acceptor are reported (see Scheme 1). Among them, the X-ray structures of compounds **1** and **2** are described. All these compounds show blue–violet or blue TPEF.

☆ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.04.006.

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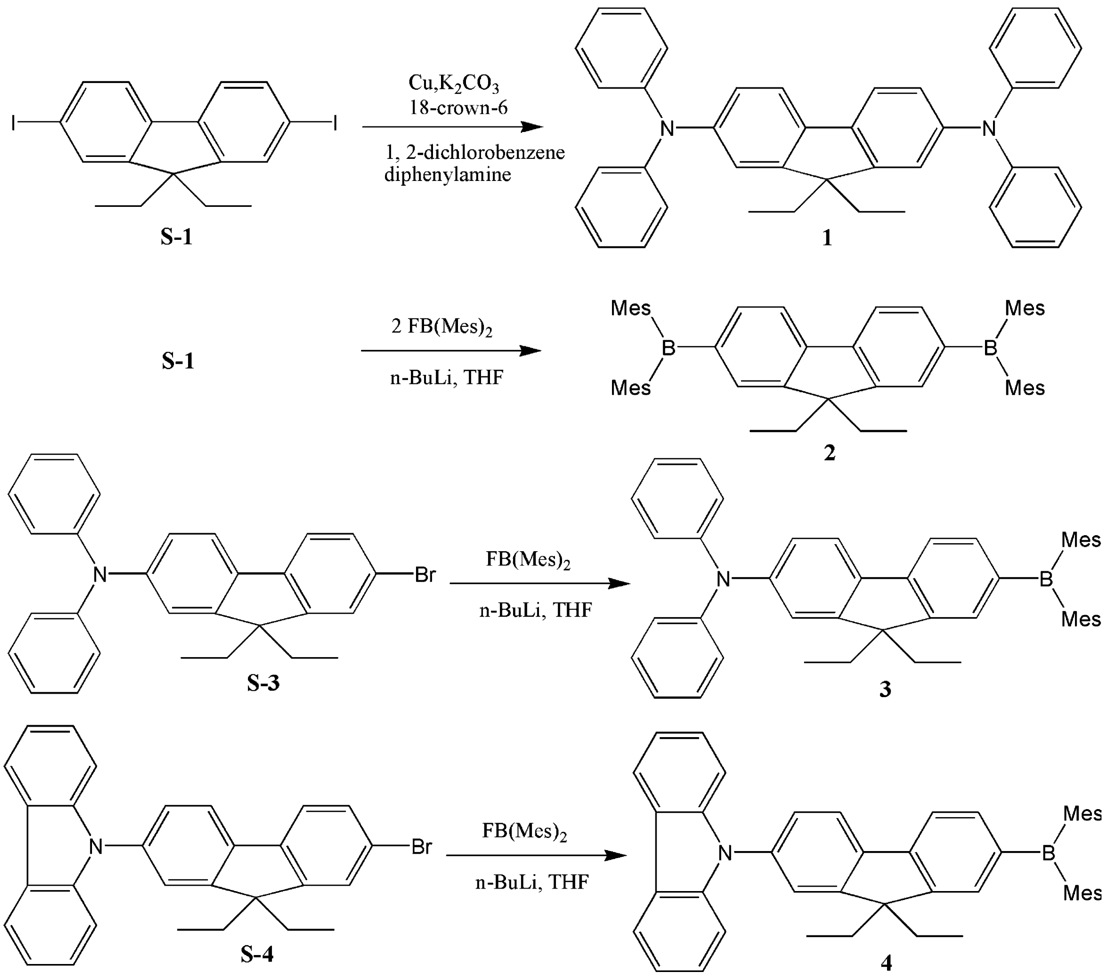


Scheme 1. Synthetic routes of the title compounds (Mes = 2,4,6-trimethylphenyl).

2. Experimental

Nuclear magnetic resonance spectra were recorded on a Brucker AM-500 spectrometer. Mass spectra were obtained on an Agilent 5973N MSD spectrometer. Elemental analyses were carried out on a PE 2400 autoanalyzer. The melting points were measured on a Mettler–Toledo DSC822e Differential Scanning Calorimeter.

The synthetic routes of these compounds are shown in Scheme 1. **S-1** (prepared from fluorene via diethylation and diiodination) with two equivalent diphenylamine via Cu-mediated Ullmann condensation afforded D-π-D type of **1**. A-π-A type of **2** was prepared by substitution of 2,7-diiodo atoms on **S-1** using dimesitylboryl groups in the presence of *n*-butyllithium at low temperature (−78 °C). **S-3** and **S-4**, the precursors of **3** and **4**, respectively, were prepared in four steps from fluorene via diethylation, bromination, iodination and Cu-mediated Ullmann condensation. Substitution of 7-bromo atom on **S-3** and **S-4** by dimesitylboryl group provided the target D-π-A type of compounds **3** and **4**. Single crystals of **1** and **2** were obtained from chloroform-petroleum ether by slow diffusion method and the structures were determined by four-circle X-ray diffraction. All the compounds are stable in air and in common organic solvents. Satisfactory ^{1}H NMR, UV spectroscopy, MS spectrometry and elemental analysis results were obtained.

*2.1. 2,7-bis(N,N-diphenylamino)-9,9-diethyl-fluorene (**1**)*

Melting point 212–213 °C, ^{1}H NMR (CDCl$_3$), δ (ppm): 0.38 (t, 6H, $J = 7.3$ Hz), 1.81 (q, 4H, $J = 7.3$ Hz), 7.05–7.77(m, 26H). MS: m/z (%) 556 (M$^+$, 100), 278 (M^{2+}, 15). Elemental Anal. Calc. for $C_{41}H_{36}N_2$: C, 88.45; H, 6.52; N, 5.03. Found: C, 88.17; H, 6.44; N, 5.01%.

*2.2. 2,7-bis(dimesitylboryl)-9,9-diethyl-fluorene (**2**)*

Melting point 237–238 °C, ^{1}H NMR (CDCl$_3$), δ (ppm): 0.23 (t, 6H, $J = 7.2$ Hz), 1.95 (q, 4H, $J = 7.3$ Hz), 2.02 (s, 24H), 2.33 (s, 12H), 6.84 (s, 8H), 7.49 (s, 2H), 7.51 (d, 2H, $J = 7.6$ Hz), 7.72 (d, 2H, $J = 7.6$ Hz) MS: m/z (%) 718 (M$^+$, 45), 248 ([B(Mes)$_2$]$^+$, 100). Elemental Anal. Calc. for $C_{53}H_{60}B_2$: C, 88.58; H, 8.41. Found: C, 88.42; H, 8.52%.

2.3. 2-(N,N-diphenylamino)-7-dimesitylboryl-9,9-diethyl-fluorene (3)

Melting point 217–218 °C, ^1H NMR ($CDCl_3$), δ (ppm): 0.30 (t, 6H, $J = 7.3$ Hz), 1.87 (q, 4H, $J = 7.8$ Hz), 2.01 (s, 12H), 2.31 (s, 6H), 6.81 (s, 4H), 7.13–7.64 (m, 16H). MS: m/z (%) 637 (M^+, 100). Elemental Anal. Calc. for $C_{47}H_{48}BN$: C, 88.52; H, 7.59; N, 2.20. Found: C, 88.34; H, 7.48; N, 2.28%.

2.4. 2-N-carbazolyl-7-dimesitylboryl-9,9-diethyl-fluorene (4)

Melting point 262–263 °C, ^1H NMR ($CDCl_3$), δ (ppm): 0.40 (t, 6H, $J = 7.3$ Hz), 2.05 (q, 4H, $J = 7.5$ Hz), 2.06 (s, 12H), 2.35 (s, 6H), 6.86 (s, 4H), 7.31 (s, 2H), 7.43 (s, 4H), 7.53–7.58 (m, 4H), 7.76 (d, 1H, $J = 7.5$ Hz), 7.97 (d, 1H, $J = 7.9$ Hz), 8.18 (d, 2H, $J = 7.7$ Hz). MS: m/z (%) 635 (M^+, 100), 515 ($(M\text{-Mes})^+$, 33). Elemental Anal. Calc. for $C_{47}H_{46}BN$: C, 88.80; H, 7.29; N, 2.20. Found: C, 88.57; H, 7.21; N, 2.09%.

*Crystal data for **1***: $C_{41}H_{36}N_2$, $M = 556.72$, monoclinic, space group $C2/c$, $a = 28.649(4)$, $b = 8.5111(9)$, $c = 27.012(4)$ Å, $\beta = 100.982(11)°$, $V = 6465.7(14)$ Å^3, $Z = 8$, $T = 293(2)$ K, $D_c = 1.144$ g cm^{-3}, $\mu = 0.066$ mm^{-1}, $R_1 = 0.0581$, $wR_2 = 0.1538$. *Crystal data* for **2**: $C_{53}H_{60}B_2 \cdot 3H_2O$, $M = 772.68$, triclinic, space group $P\bar{1}$, $a = 8.6055(15)$, $b = 17.581(3)$, $c = 17.976(3)$ Å, $\alpha = 114.075(9)$, $\beta = 101.569(10)$, $\gamma = 94.756(11)°$, $V = 2390.9(6)$ Å^3, $Z = 2$, $T = 293(2)$ K, $D_c = 1.073$ g cm^{-3}, $\mu = 0.064$ mm^{-1}, $R_1 = 0.1042$, $wR_2 = 0.2470$.

We performed DFT (density functional theory) quantum chemical calculations on **1** and **2** by using Gaussian 03 [7]. The functional used includes Becke's [8] three parameter hybrid functional in conjunction with the Lee–Yang–Parr [9] correlation functional, which is abbreviated as B3LYP. The calculations were performed using the valence triple-zeta basis sets 6-311G augmented with a set of polarization and diffuse functions at the non-hydrogen atoms since the studied compounds are π-delocalization systems [10]. The basis set 6-311+G* was used throughout this study. HOMO and LUMO of the compounds studied are obtained using the visuallization package GaussView [11].

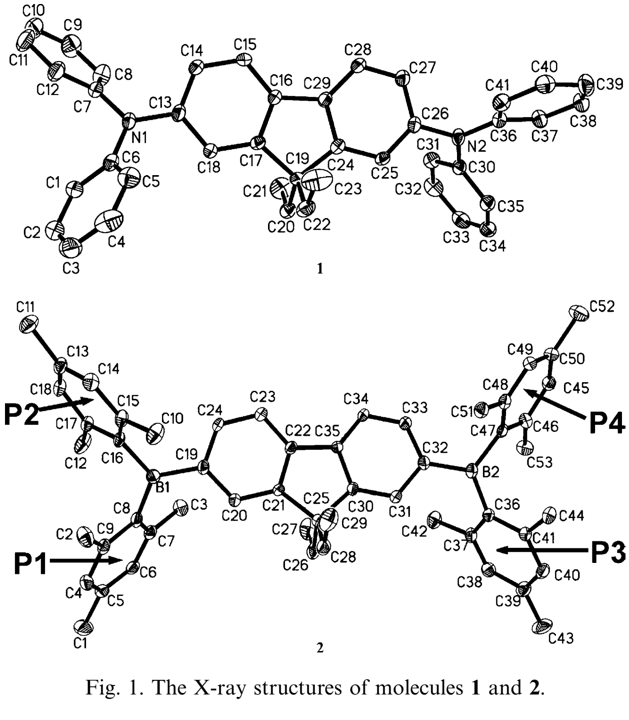
Linear absorption spectra were recorded on a PE lambda 35 UV-VIS spectrophotometer. Single-photon excited fluorescence (SPEF) spectra were measured on an Edinburgh FLS920 fluorescence spectrometer. TPEF spectra were performed on a Ti:sapphire femtosecond laser (Coherent, Mira 900-D) with a pulsewidth of 200 fs and a repetition rate of 76 MHz as pump source and with a streak camera (Hamamatsu, C5680) in conjunction with an imaging spectrography (Hamamatsu, C5094) as recorder. TPEF was collected at a direction perpendicular to the pump beam.

3. Results and discussion

As shown in Fig. 1, terminal diphenylamino or dimesitylboryl of **1** or **2** are arranged in propeller-like fashion. The planarity of the fluorenyl π-bridge is satisfactory with the dihedral angle between the two constituent phenyl rings only 3.0° and 6.2° for **1** and **2**, respectively. BC_3 cores and NC_3 cores are perfectly planar with the sum of angles around N or B atoms 360.0(2)° for **1**, 359.8(6)° and 359.9(6)° for **2** and with the maximal deviation of B(N) atom to the C_3 plane being only 0.0339 Å.

The dihedral angles of **2** between BC_3 planes and fluorenyl plane (32.7° and 21.2°, respectively) are distinctly smaller than those (51.8°, 54.9°, 54.0° and 53.7°) between BC_3 planes and terminal phenyls (P1, P2, P3 and P4, respectively). Fluorenyl relevant B–C bond lengths (B1–C19 = 1.557(10) and B2–C32 = 1.557(10) Å) are considerable shorter than mesityl relevant B–C bond lengths (B1–C8 = 1.571(11), B1–C16 = 1.575(7) Å and B2–C36 = 1.571(11), B2–C47 = 1.592(10) Å). The above structural features indicate that the BC_3 moiety is more π-conjugated with fluorenyl group in comparison with terminal phenyl rings.

Fig. 2 shows that **2** has a quadrupolar charge transfer from the central fluorenyl to the boron atoms upon excitation from HOMO to LUMO, indicating its A-π-A characteristic at the excited state. For **1**, similar symmetric charge transfer happens upon excitation from



1

2

Fig. 1. The X-ray structures of molecules **1** and **2**.

HOMO to LUMO, but inversely, from the two terminal diphenylamino to the central fluorenyl (see Fig. 3), indicating a D-π-D feature of its excited state.

The TPEF cross-section σ_e and two-photon absorption (TPA) cross-section σ are obtained by two-photon fluorescence method according to following equations [12]:

$$\sigma_e = \sigma_{e,r}\frac{Fn_r}{F_r n},$$

$$\sigma = \frac{\sigma_e}{\Phi'}.$$

In above equations, F stands for integral fluorescence intensity, n for refractive index, and the subscript r indicates the quantities of the reference (Coumarin 307 was used as reference). Φ' is the TPEF quantum yield, which is usually supposed to be the same as the SPEF quantum yield [12].

As shown in Table 1 and Fig. 4, TPEF peak positions of all these compounds are slightly red-shifted relative to that of their corresponding SPEF spectra, which may result from re-absorption effect in concentrated solution.

The SPEF and TPEF of **1** and **2** are located in blue-violet spectral region. Compared with D-π-D molecule **1**, A-π-A molecule **2** shows better SPEF properties, such as enhanced quantum yield and a 14 nm blue-shift of the emission peak. The TPEF spectrum of **2** also has a 13 nm blue-shift in comparison with that of **1**. To our knowledge, the λ_{max} of TPEF (405 nm) of **2** is one of the shortest reported. This indicates that dimesitylboryl acceptor is a SPEF fluorophore and a blue-shift group. However, the TPEF cross-section of **2** is slightly smaller than that of **1** at $\lambda_{ex} = 730$ nm. Compound **1** shows smaller TPA cross-sections σ relative to that of similar compounds [13], which may be due to the 730 nm laser beam is away from the optimal two-photon excitation wavelength. For some symmetric TPEF active molecules, TPA peak was reported to be at much shorter wavelength than twice of that of linear absorption [5,13–16].

D-π-A compounds **3** and **4** show much enhanced TPEF intensities at $\lambda_{ex} = 730$ nm, with their σ_e and σ values being one order of magnitude that of symmetric **1** of D-π-D type and **2** of A-π-A type. In fact, the σ_e and σ

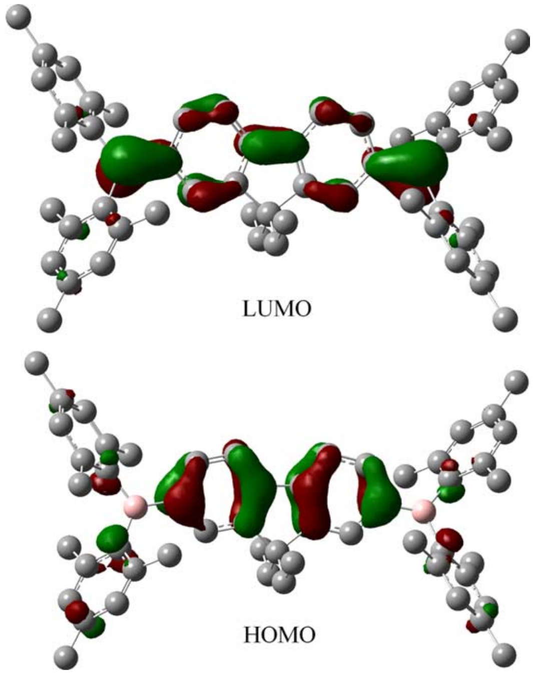


Fig. 2. The electron density distribution of the frontier molecular orbitals of A-π-A compound **2**.

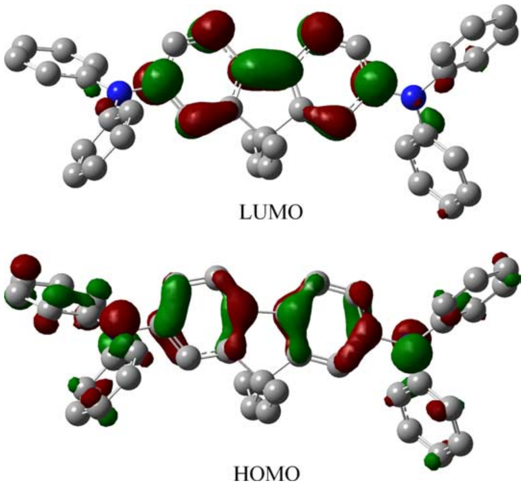


Fig. 3. The electron density distribution of the frontier orbitals of D-π-D compound **1**.

Table 1
The photophysical properties of compounds **1**–**4** in THF

	λ_{abs} (nm)[a]	λ_{SPEF} (nm)[a]	Φ[b]	τ (ns)	λ_{TPEF} (nm)[c]	σ_e[d] (GM)[e]	σ[d] (GM)[e]
1	375	397, 417	0.36	1.0	418	5.4	15
2	371	384, 403	0.52	1.1	405	4.1	8
3	400	482	0.59	2.5	484	43, 251[f]	73, 425[f]
4	355	435	0.67	2.2	440	78	116

[a] Linear absorption and SPEF maxima with $C = 1.0 \times 10^{-5}$ M.

[b] Fluorescence quantum yields determined using coumarin 307 as standard [17].

[c] TPEF maxima with $C = 5.0 \times 10^{-3}$ M.

[d] TPEF cross-section (σ_e) and TPA cross-section (σ) at $\lambda_{ex} = 730$ nm.

[e] 1 GM = 10^{-50} cm^4 s photon^{-1} molecule^{-1}.

[f] Values at $\lambda_{ex} = 800$ nm.

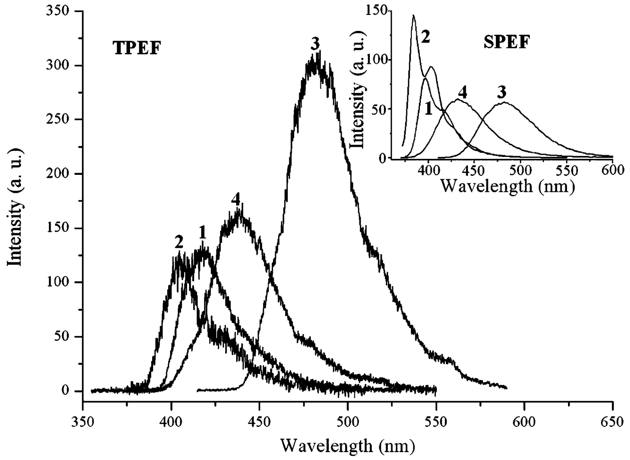


Fig. 4. Single-photon excited fluorescence (SPEF) spectra with $C = 1.0 \times 10^{-5}$ M and two-photon excited fluorescence (TPEF) spectra (excited at 730 nm for **1**, **2** and **4**; 800 nm for **3**) with $C = 5.0 \times 10^{-3}$ M in THF. The intensity scales of TPEF of **1** and **2** have been expanded by 10 times.

values of **3** can be further augmented several times under a more favorable excitation at $\lambda_{ex} = 800$ nm (see Table 1). On the other hand, as a trade-off, the spectra of **3** and **4** (see λ_{max} of absorption, SPEF and TPEF peaks) are considerably red-shifted. However, their TPEF as well as SPEF are still located in blue region.

Compound **4** possesses the highest quantum yield and the strongest TPEF intensity at $\lambda_{ex} = 730$ nm. Compared with **3**, all spectra of **4** are more blue, which may be due to the weaker electron-donating ability of carbazolyl group relative to diphenylamino group.

4. Conclusions

Four symmetric and unsymmetric fluorenyl derivatives, with dimesitylboryl group as electron acceptor and diphenylamino group (or carbazolyl group) as electron donor, have been synthesized. All these compounds show blue–violet or blue two-photon excited fluorescence (TPEF) demenstrating that dimesitylboryl group is a good fluorophore and a blue-shift group. Compounds **1** and **2** show quasi-symmetric and π-conjugated structure at the ground state (revealed by X ray structure determinations). Upon excitation to the excited state, quadrupolar charge transfer takes place for **1** and **2** (indicated by DFT quantum chemical calculations). These geormetric and electronic structure features may have a close relationship to their TPEF properties.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with Cambridge Crystallographic Data Centre, CCDC No. 224882 for **1** and 224881 for **2**. 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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