Nonvolatile liquid anthracenes for facile full-colour luminescence tuning at single blue-light excitation

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Nonvolatile room-temperature luminescent molecular liquids are a new generation of organic soft materials. They possess high stability, versatile optical properties, solvent-free fluid behaviour and can effectively accommodate dopant dye molecules. Here we introduce an approach to optimize anthracene-based liquid materials, focussing on enhanced stability, fluorescence quantum yield, colour tunability and processability, with a view to flexible electronic applications. Enveloping the anthracene core in low-viscosity branched aliphatic chains results in stable, nonvolatile, emissive liquid materials. Up to 96% efficient energy-transfer-assisted tunable emission is achieved by doping a minute amount of acceptor dye in the solvent-free state. Furthermore, we use a thermoresponsive dopant to impart thermally controllable luminescence colours. The introduced strategy leading to diverse luminescence colours at a single blue-light excitation can be an innovative replacement for currently used luminescent materials, providing useful continuous emissive layers in developing foldable devices.
Materials with tunable colours continue to fascinate mankind, and stable, colourful and emissive materials\(^1\) have many potential applications. At the same time, these materials are key to new research aimed at generating low cost and energy-saving light sources\(^2\). Advanced organic synthetic methodologies have been extensively used to develop new chemicals with improved quantum efficiency. However, finding simple and controllable methods to process these emissive organic materials remains a major challenge\(^1\). In addition, \(\pi\)-conjugated molecules inherently aggregate, leading to optical and electronic properties that vary drastically according to the local environment of the \(\pi\)-conjugated core and applied conditions. Because the materialization of uninterrupted emissive layers using paintable organic liquids has yet to be realized, reliable emissive materials that can maintain continuous active layers when bent and folded\(^3\) are required for the future prospects of flexible devices\(^4\). Newly developed, stable and emissive liquid materials could be potential candidates for this goal. It is also important to simply demonstrate how a full range of coloured emission can be obtained without much synthetic effort, for example, by doping (dissolving) minute amounts of dyes into the emissive liquid.

Small aromatic molecules such as anthracenes are extensively studied for organic electronics because of the charge-carrier mobility of their ordered assemblies\(^7\), high quantum yield and blue emissive features\(^9\). Despite this, their sensitivity to air and light\(^10\) and the inherent difficulty of preparing homogeneous thin films from their crystalline assemblies, while retaining high quantum yields\(^11\) and a diversity in luminescence colour\(^12\), are still major drawbacks. In this context, a new approach that can overcome all these issues is highly desirable. A nonvolatile, low-viscosity and highly emissive room-temperature liquid material is a promising candidate. We prepared oligo(\(p\)-phenylenevinylene)-based blue-emitting solvent-free liquids by isolating the \(\pi\)-conjugated oligo(\(p\)-phenylenevinylene) core using bulky and soft aliphatic chains. These were used as a matrix/solvent to produce white light-emitting paints\(^13\). The advantage of functional molecular liquids is their ability to retain the features of isolated optoelectronically active \(\pi\)-conjugated moieties in the bulk fluid state. In this respect, there is a clear difference between the above-mentioned liquids\(^13\) and other amorphous organic fluids that have been obtained by merely lowering the glass-transition temperature\(^14\)–\(^16\).

Here, by attaching branched low-viscosity aliphatic chains to the anthracene core, we report nonvolatile, blue-emitting and highly stable room-temperature liquid anthracenes into which acceptor dyes can be doped to tune the luminescence colour. The dye-doped anthracene liquid exhibits a variance in luminescence covering almost the entire visible range. This ease of luminescence colour tuning and the liquid features of the blends pave a practical way towards reliable emissive materials capable of forming facile coatings and acting as a continuous active layer in flexible devices.

Results

Synthesis and characterization of anthracene liquids. This study presents a versatile approach that makes use of the high photostability, fluorescence quantum yield and colour tunability of anthracene derivatives to design novel light-emitting liquid materials. As depicted in Fig. 1, we have synthesized two new anthracene derivatives (1 and 2). The anthracene derivatives 1 and 2 were obtained as yellowish transparent viscous fluids at room temperature, whereas the reference molecule 3 was a pasty solid. All anthracenes were unambiguously characterized by ultraviolet-visible absorption, steady-state fluorescence, \(^1\)H, \(^{13}\)C NMR and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI–TOF MS).

The \(^1\)H NMR (Supplementary Figs S1 and S2) and thermogravimetric analysis (TGA) (Supplementary Fig. S3) indicated an absence of residual solvent in the bulk fluid sample. Swallow-tail type aliphatic chains attached to a dendritic skeleton of the phenyl substituent and hyperbranched aliphatic chains without the dendritic skeleton were used in 1 and 2 respectively, to ensure significant fluidity\(^17\) at room temperature. On the other hand, linear aliphatic chains present in 3 imparted solid features at room temperature, emphasising the importance of branched alkyl chains in obtaining solvent-free liquids at room temperature. In the cooling trace of the differential scanning calorimetry (DSC) thermogram, 1 exhibits a glass-transition temperature \((T_g)\) of \(-59.6^\circ C\) \((\text{molar heat capacity } C_{\text{mol}} 1955.1 \text{ J mol}^{-1} \text{K}^{-1})\), which is increased to \(-32.4^\circ C\) \((C_{\text{mol}} 389.6 \text{ J mol}^{-1} \text{K}^{-1})\) for 2 (Fig. 2a). Both molecules exist in the solvent-free fluid state over a wide range of temperatures up to around 350 °C (Supplementary Fig. S3). In the X-ray diffraction (XRD) analysis, 1 and 2 both exhibit a halo in the wide angle region corresponding to an average distance between the molten aliphatic chains of 4.5 Å for 1 \((q = 1.4 Å^{-1})\) and 4.8 Å for 2 \((q = 1.3 Å^{-1})\), respectively (Fig. 2b, Supplementary Fig. S4). The disordered anthracene core–core distance of around 21 Å for 1 and 17 Å for 2 appeared as a broad halo at smaller \(q\) in both the XRD \((q = 0.30 Å^{-1} \text{ for 1 and 0.36 Å}^{-1} \text{ for 2})\) and small-angle X-ray scattering (inset of Fig. 2b) \((q = 0.30 Å^{-1} \text{ for 1 and 0.34 Å}^{-1} \text{ for 2})\) results. This distance is larger than 1 for 2 because of the presence of bulkier substituents around the anthracene core (for example, schematic illustration in Supplementary Fig. S4c). In rheology experiments, the loss modulus \(G''\) is found to be higher than the storage modulus \(G'\) over the measured angular frequency range of \(\omega = 0.1–100 \text{ rad s}^{-1}\) and for a shear strain of \(\gamma = 0.1\%\) (Fig. 2c), indicating liquid behaviour. In addition, a significant reduction in complex viscosity \((\eta^* )\) was observed from 84.0 (2) to 0.28 Pa s (1) at \(\omega = 10 \text{ rad s}^{-1}\) (Fig. 2d, Supplementary Table S1). In conclusion, \(^1\)H NMR, TGA, DSC, XRD, small-angle X-ray scattering and rheology experiments confirmed the solvent-free liquid characteristics of anthracenes 1 and 2.

Photostability studies. StERIC hindrance via soft and bulky tail attachment can disturb intermolecular \(\pi\)-\(\pi\) interactions among adjacent anthracene units\(^8\),\(^9\) in the solvent-free liquid state and improve the photostability. To demonstrate this, photo-stability studies have been carried out by irradiating the samples at 365 nm (100 W m\(^{-2}\)) using a Xe lamp. In comparison with cast thin film of 9,10-diphenylanthracene 4 (Fig. 1, Supplementary Figs S5 and S6), the liquid anthracenes exhibited a remarkable improvement in stability (Supplementary Fig. S7). As shown in Fig. 3, 1 was optically active for up to 4 h under irradiation in the solvent-free state and 15 h in dilute dichloromethane solution. In comparison, the characteristic absorption (375 nm, Supplementary Fig. S5a) and emission (430 nm, Fig. 3a) peaks of the anthracene chromophore of 4 in solution had completely disappeared after just 2 h (Supplementary Figs S5 and S6). This could be attributed to conversion of the anthracene unit into 9,10-endoperoxides upon irradiation\(^20\). The \(^1\)H resonance characteristics of the parent anthracene protons exhibited significant changes upon irradiation (Supplementary Fig. S8). The formation of a photo-oxidized 9,10-endoperoxide on 1 was confirmed by the appearance of a peak at 84.5 p.p.m. in \(^{13}\)C NMR analysis (Supplementary Fig. S9a)\(^20\),\(^21\). The 9,10-endoperoxide was also formed by 4 under the same experimental conditions (Supplementary Fig. S9b). The failure of the [4 + 2] Diels–Alder cycloaddition\(^22\) between fullerene \(C_{60}\) and
liquid anthracenes also supports the enhanced stability of these materials. The pronounced stability of liquid anthracenes is directly related to the enveloping of the anthracene core by bulky branched alkyl chains to reduce the attack by oxygen and dimerization of the core.

Optical features of monomer-like bulk liquids. To understand how effectively the core is isolated in the solvent-free liquids, absorption and emission spectra of 1 and 2 (Fig. 4, Supplementary Fig. S10) were compared in the solvent-free state and dilute solution. Intermolecular interactions of the anthracene core are almost completely prevented, and monomeric features identical to those in dilute dichloromethane solutions are retained in the dense bulk liquid state. Despite a longer wavelength tail appearing in the absorption spectra in the solvent-free state, which is likely to be caused by scattering from the surface, the emission features are identical in both cases. The yellowish, transparent liquid of 2 under visible light (Fig. 4c) exhibits a strong blue emission under ultraviolet light ($\lambda_{ex} = 365$ nm, Fig. 4d). The blue-emitting anthracene liquids (1 and 2) exhibit high absolute fluorescence quantum yields of ca. 55% in solvent-free thin films under ambient conditions (Supplementary Table S1). These are somewhat lower than the values obtained for the dilute dichloromethane solutions (Supplementary Table S2), but still relatively high for solid or film states of anthracenes\textsuperscript{23}. Values for the absolute fluorescence quantum yield at liquid nitrogen temperature and refractive index values of the derivatives are summarized in Supplementary Table S1. The ultraviolet-visible absorption, steady-state fluorescence and photoconductivity measurements (Supplementary Fig. S11) highlight the importance of our design strategy to yield room-temperature liquids by enveloping each core with branched alkyl chains to reduce the intermolecular core-core interactions. This core isolation strategy enables the intrinsic monomeric characteristics of a \( \pi \)-conjugated core unit to be achieved in bulk, solvent-free liquid matter.

Energy transfer with minute doping. In contrast to previously reported organic luminescent materials that have substantially...

**Figure 1** | Molecular structure of anthracenes and dopants. The figure shows the chemical structure of anthracenes (1-4) and dopants (D1 and D2) used in this study.

**Figure 2** | Characterization of solvent-free room-temperature liquid anthracenes. (a) DSC thermograms in the cooling trace showing the glass-transition temperatures ($T_g$). (b) XRD diagrams with small-angle X-ray scattering profiles as insets, variation of (c) storage modulus ($G'$)(circles) and loss modulus ($G''$) (squares), as well as (d) complex viscosity ($\eta^*$), (diamonds) versus angular frequency on double logarithmic scale, of 1 (blue markers) and 2 (red markers).
Comparison of the variation of (a) fluorescence intensity at 430 nm in solvent-free states of 1 and 4 (Solvent-free, Film) supported on a quartz plate and in dichloromethane solution (Solution) (c = 1 × 10^{-4} M, l = 1 mm, λ_{ex} = 375 nm) of 1 and 4. (b) Variation of the $^1$H NMR peak area of aromatic protons of 1 (7.7 p.p.m.) and 4 (7.5 p.p.m.) in dichloromethane-d$_2$.

Figure 4 | Optical features of liquid anthracenes. Comparison of the normalized (a) absorption and (b) fluorescence spectra of 1 and 2 in a solvent-free bulk liquid state (solvent-free) supported on a quartz plate at room temperature and in dichloromethane solution (Solution) (c = 5 × 10^{-5} M, l = 1 mm, λ_{ex} = 375 nm). Photographs of 2 under (c) visible and (d) ultraviolet light (365 nm).

(reduced quantum efficiency in the solvent-free solid or film state, high quantum yields have been achieved by these luminescent solvent-free liquids. A long-standing problem with organic materials has thereby been solved through this alternative route. A further development is to manipulate the luminescence colour in a facile and cost-effective way. Recently, organic materials with tunable luminescence behaviour have gained much attention. Among those systems, energy transfer assisted light harvesting materials has thereby been solved through this alternative route. In energy transfer, 95% fluorescence quenching of 1 and efficient energy transfer to D1 was observed for only 0.3 mol% of D1 (Fig. 5a, Supplementary Fig. S12) when excited at 350 nm, where the D1 absorption is at a minimum. The efficiency of energy transfer is increased with increasing mol% of D1, for example, at 1.0 mol% the energy transfer efficiency was found to be 96% (Supplementary Fig. S13). The energy transfer rate was calculated to be 3.75 × 10^{14} s^{-1} with a Förster distance (R_0), at which the energy-transfer efficiency becomes 50%, of 44 Å. Under these conditions, 100% fluorescence enhancement was observed for D1 at 475 nm, when compared with the direct excitation of D1 at 440 nm in the donor matrix (Supplementary Fig. S13). The excitation spectrum of the energy-transfer system monitored at 475 nm revealed a relatively low contribution from the direct excitation of D1 (Supplementary Fig. S13). Interestingly, at higher mol%, acceptor D1 tends to aggregate in the donor scaffold, and energy is transferred to both monomers and aggregates of D1.

The energy transfer was further confirmed by fluorescence lifetime decay profiles of 1 monitored at 430 nm in the absence and presence of D1 (Fig. 5b). The fluorescence decay profile of 1 exhibited a biexponential decay with components having lifetimes of 5.8 (98%) and 0.35 ns (2%). As the concentration of D1 is increased, a triexponential decay with lifetimes of 4.3 (33%), 0.13 (64%) and 0.22 ns (3%) at 0.3 mol% of D1, and further 3.5 (18%), 1.84 (75%) and 0.29 ns (7%) at 0.5 mol% of D1, were observed. Such a decrease of the anthracene donor lifetime in presence of the acceptor is direct evidence of the fluorescence resonance energy transfer. As additional evidence for energy transfer, a temporal growth in the emission of the acceptor when excited at 377 nm into the donor matrix (Fig. 5b, inset) was observed. The requirement of just 0.3 mol% of acceptor for efficient energy transfer is the lowest quantity reported for any supramolecular energy transfer system. One possible reason for the increased efficiency at low acceptor loading could be the presence of small clusters in the monomer-like bulk liquid donor. Such an energy transfer in disordered aggregates is well documented. The structural similarity and ease of trapping of the acceptor molecules in these small clusters results in efficient energy transfer.

The structural similarity and ease of trapping of the acceptor molecules in these small clusters results in efficient energy transfer.
Figure 5 | Energy-transfer-assisted tunable emission. (a) Normalized emission spectral changes of 1 upon increasing the concentration of D1 (λex = 350 nm). (b) Emission lifetime decay profile of 1 (blue squares) (λex = 377 nm) in the presence of 0.3 (orange squares) and 0.5 mol% (pink squares) of D1 monitored at 430 nm supported on quartz plate, and inset shows the decay profiles of D1 (0.3 mol%) in the matrix of 1 (red squares) and D1 alone (blue squares), monitored at 475 nm (λex = 377 nm). IRF corresponds to Instrument Response Function. (c) Photographs of the luminescent thin films of 1 (i) and 1 doped with D1 (ii–v), which are correlated to the emission spectra of (a).

Thermoresponsive features of solvent-free composites. To extend the tunable emission features, we monitored the luminescence changes of 1 by adding D2 (Supplementary Fig. S14, composites denoted as vi–x). Upon addition of D2, the intensity of the 0-0 vibronic band in the fluorescence spectrum of 1 was decreased with an accompanying increase in the D2 emission intensity when excited at 375 nm, indicating the possibility of a weak energy transfer from 1 to D2. A violet colour at 2 mol% (Fig. 6a (vi)) and purple colour at 5 mol% (Fig. 6a (vii)) of D2 was observed. A combination of 0.5 mol% D1 and 5 mol% D2 resulted in a red emission (Fig. 6a (xi)). The temperature dependent emission of europium complexes (for example, D2) has been extensively studied and this property has been used for various sensing applications\(^5\). Here the thermoresponsivity of D2 enables luminescence modulation of the liquid composite. On increasing the temperature, the red emission colour was changed to yellow at around 50 °C (Fig. 6a (xiii)) and to emerald green after a further increase in temperature (Fig. 6a (xv)), which is mostly contributed by the luminescence of D2. The fluorescence spectra upon heating (Fig. 6b) and cooling (Supplementary Fig. S14) between 20 and 100 °C, exhibited reversible changes, especially between 600 and 640 nm.

The thermoresponsive liquid composite behaves as a thermometer with reversible luminescence colour variation\(^36\). Because the emission centred at 610 nm is thermally gated, the liquid composite exhibits temperature controlled luminescence tuning with attractive colours. Although the triexponential lifetime of 1 in the composite showed a drastic decrease to 2.1 ns (39%), 0.9 ns (50%) and 0.24 ps (11%) (Supplementary Fig. S14), a clear picture of the electronic communication between 1, D1 and D2 is not available because there is a possibility of direct excitation of D2 at 375 nm. However, the excitation spectrum of the composite monitored at 610 nm reveals contributions from 1 and D1 (Supplementary Fig. S14)\(^37\). Hence, the thermoresponsive features of D2 enabled manipulation of various luminescence colours (Fig. 6c, Supplementary Table S3). The resulting tunable composite system obtained by mixing two dopants with liquid 1 in specific ratios retained fluid characteristics (Supplementary Fig. S15), making room for further diversification of colour obtainable at single ultraviolet wavelength excitation.

Discussion

Blue-emitting, nonvolatile, low-viscosity, room-temperature anthracene liquids, devoid of various disadvantages of the currently available anthracene-based organic functional materials, have been synthesized. The liquid anthracenes have a high fluorescence quantum yield and exhibit improved photostability under ambient conditions. The very low viscosity of these emissive liquids allows doping of other emissive and thermoresponsive components into the liquid matrix, leading to a tunable luminescence colour. The most efficient energy transfer from an anthracene unit to any dopant and the controllable thermoresponsive luminescence colour changes in the absence of solvent are both new phenomena. The liquid composite with a...
range of reversible luminescence colours covering almost the whole visible spectrum can also be used as a colour-indicating thermometer. This facile luminescence variation has strong advantages over other reported methods using either complex synthesis or multicomponent systems. Our rational design allows the production of enriched liquid matter, which provides technological potential for a continuous active layer in flexible materials. We therefore believe that these materials will be promising candidate with many opportunities to design low-cost, environmentally-friendly, flexible, foldable luminescent products.

Methods

Materials. Unless otherwise stated, all starting materials and reagents were purchased from commercial suppliers and used without further purification. The hyperbranched alcohol Fine Oxocol 180N, containing isomers, was gifted by Nissan Chemical Industries, Ltd., Japan, and converted to the bromo derivative.

Synthesis and characterization of 1–3. In a general synthetic procedure (Supplementary Methods), a mixture of 9,10-bis(3,5-dihydroxyphenyl)anthracene (Aldrich) were used as dopants. Tris(1,3-diphenyl-1,3-propanedionato)(1,10-phenanthroline)europium(III) and Nissan Chemical Industries, Ltd., Japan, and converted to the bromo derivative. Hyperbranched alcohol Fine Oxocol 180N, containing isomers, was gifted by Nissan Chemical Industries, Ltd., Japan, and converted to the bromo derivative.

Figure 6 | Tunable emission colours from liquid composites. (a) Photographs of the luminescence colour tunability and thermoresponsive feature of the composites of 1, D1 (0.5 mol%) and D2 (5 mol%). (b) Thermoresponsive luminescence spectral changes of the composite of 1, D1 and D2, supported on a quartz plate (λex = 375 nm) upon heating; inset shows the corresponding emission changes from 600 to 640 nm. (c) Commission internationale de l’éclairage coordinate values of the overall colour tunability achieved by doping of 1 with D1 and/or D2, as well as with temperature. The Commission internationale de l’éclairage coordinate also includes 2. The indications of i–v are from the composites of 1 and D1 (Fig. 5), vi–x are from the composites of 1 and D2 (Supplementary Fig. S14a) and xi–xv are from composites of 1, D1 and D2 (b).

Measurements. 1H NMR (600 MHz) spectra were measured with a Bruker Biospin DRX-600 spectrometer, and 13C NMR (75 MHz) spectra were recorded on a JEOL model AL300 spectrometer using TMS as internal standard. MALDI–TOF MS (matrix-dithranol) were obtained by a Shimadzu AXIMA-CFR Plus station using dithranol as the matrix. Ultraviolet-visible absorption and fluorescence spectra in solution and solvent-free liquid states were recorded on a Hitachi U-2910 spectrophotometer.

Transparent yellowish liquid (yield, 50%). TC: 10°C (20%); 50°C (15%) (Fig. 5), vi–x are from the composites of 1 and D2 (Supplementary Fig. S14a) and xi–xv are from composites of 1, D1 and D2 (b). 1H NMR (400 MHz, CDCl3): δ = 7.75–7.80 (m, 4H, Ar), 7.30–7.36 (m, 4H, Ar), 7.07–7.12 (s, 4H, Ar), 6.85–6.88 (s, 2H, Ar), 6.80–6.84 (m, 8H, Ar), 6.74–6.77 (s, 4H, Ar), 5.11–5.16 (m, 8H, O-CH2-Ar), 3.75–3.85 (m, 16H, OCH2), 1.70–1.85 (s, 8H, CH(CH3)2), 1.05–1.53 (m, 256H, CH2), 0.80–0.95 (m, 48H, CH2), 1C NMR (75 MHz, CDCl3): δ = 154.0, 151.3, 141.6, 137.6, 130.2, 127.6, 127.1, 125.6, 115.9, 114.7, 112.9, 110.9, 101.9, 71.9, 65.7, 38.6, 32.4, 31.8, 30.2, 27.3, 23.2, 14.4; MALDI–TOF MS (matrix-dithranol): calculated for C98H162O4 1,404.33, found 1,403.40 [M + H].

1.25–1.45 (m, 80H, CH2), 1.05–1.22 (m, 8H, CH(CH3)2), 0.78–0.89 (m, 48H, CH2), 13C NMR (75 MHz, CDCl3): δ = 141.5, 137.9, 130.2, 127.6, 125.7, 110.4, 101.4, 71.9, 40.1, 39.9, 39.1, 38.6, 37.9, 37.8, 37.5, 37.3, 37.2, 36.8, 35.1, 35.0, 34.9, 34.0, 33.4, 32.5, 32.3, 32.2, 30.9, 30.8, 30.7, 30.5, 30.2, 30.0, 29.9, 29.8, 29.5, 28.1, 27.6, 26.1, 24.8, 23.7, 23.6, 23.5, 22.3, 22.9, 20.4, 20.0, 19.5, 19.4, 17.1, 16.9, 16.2, 15.0, 14.7, 14.5, 14.4, 14.3, 14.2, 12.6, 12.5, 11.7, 11.5, 11.2; MALDI–TOF MS (matrix-dithranol): calculated for C91H153O2 1,403.43, found 1,403.40 [M + H].

White pasty solid (yield, 57%), mp: 14–15°C. TLC (CHCl3:n-hexane, 195:5): δ = 7.60–7.85 (m, 4H, Ar), 7.36–7.42 (m, 4H, Ar), 6.66–6.67 (s, 2H, Ar), 6.60–6.65 (s, 4H, Ar), 3.84–4.05 (m, 8H, OCH2), 1.78–2.05 (m, 4H, CH(CH3)2), 1.25–1.45 (m, 80H, CH2), 1.05–1.22 (m, 8H, CH(CH3)2), 0.78–0.89 (m, 48H, CH2), 1C NMR (75 MHz, CDCl3): δ = 141.5, 137.9, 130.2, 127.6, 125.7, 110.4, 101.4, 71.9, 40.1, 39.9, 39.1, 38.6, 37.9, 37.8, 37.5, 37.3, 37.2, 36.8, 35.1, 35.0, 34.9, 34.0, 33.4, 32.5, 32.3, 32.2, 30.9, 30.8, 30.7, 30.5, 30.2, 30.0, 29.9, 29.8, 29.5, 28.1, 27.6, 26.1, 24.8, 23.7, 23.6, 23.5, 22.3, 22.9, 20.4, 20.0, 19.5, 19.4, 17.1, 16.9, 16.2, 15.0, 14.7, 14.5, 14.4, 14.3, 14.2, 12.6, 12.5, 11.7, 11.5, 11.2; MALDI–TOF MS (matrix-dithranol): calculated for C91H153O2 1,403.43, found 1,403.40 [M + H].

White pasty solid (yield, 57%), mp: 14–15°C. TLC (CHCl3:n-hexane, 95:5): δ = 0.52; 1H NMR (400 MHz, CDCl3): δ = 8.07–8.09 (m, 4H, Ar), 7.78–7.84 (m, 4H, vinyl), 7.33–7.38 (s, 2H, Ar), 6.61–6.70 (s, 4H, Ar), 3.97–4.03 (m, 8H, OCH2), 1.77–1.85 (m, 8H, CH2), 1.85–1.73 (m, 8H, CH2), 1.43–1.50 (m, 8H, CH2), 1.22–1.41 (m, 6H, CH2), 0.87–0.93 (m, 12H, CH2), 1C NMR (75 MHz, CDCl3): δ = 161.8, 161.1, 156.1, 141.6, 137.8, 130.2, 127.6, 125.7, 110.4, 101.3, 68.9, 68.5, 64.6, 32.5, 30.2, 29.7, 29.3, 29.1, 26.6, 26.3, 26.3, 23.2, 14.4; MALDI–TOF MS (matrix-dithranol): calculated for C91H153O2 1,403.43, found 1,403.40 [M + H].
and a JASCO FP-8300 spectrophotometer, respectively. The absolute quantum yields were calculated using a Hamamatsu C9220-02G instrument. Time-resolved fluorescence lifetime measurements were carried out by using time-correlated single-photon counting lifetime spectroscopy system HORIBA FluoroCube 3000U-UltraFast-SP spectrophotometer ($\lambda_{ex} = 377\mathrm{nm}$). The quality of the fit has been judged by goodness-of-fit parameters such as $r^2$ test ($<1.2$), as well as the visual inspection of the residuals. DSC and TGA were performed with a TA instruments DSC Q2000 and SH TG/DSC 8020, respectively. Refractive index measurements were carried out at 20 °C by using a Kyoto Electronics RA-600 refractometer using light-emitting diode Na-D 589.3 nm. XRD analysis was carried out using a Rigaku RINT ULTIMA + powder diffractometer with a copper K-alpha source. The photoluminescence experiments were carried out using an Arttron Paar Physica MCR301 rheometer at 20 °C by using about 1 g of the liquid samples. The irradiation of the samples at 365 nm for the stability test has been carried out using an ASAHI spectra LAX-102 compact xenon light source.

**Photocconductivity measurements.** The flash-photolysis time-resolved microwave conductivity measurement was carried out using a X-band (9 GHz) microwave circuit at low power (approximately 3 mW) and a nanosecond laser irradiation at 355 nm with photon flux of $1.8 \times 10^{15}$ photons cm$^{-2}$ pulse$^{-1}$. Flash-photolysis time-resolved microwave conductivity samples were prepared by pasting the samples on a quartz plate. The obtained transient conductivity ($\Delta \sigma$ in S m$^{-1}$) was converted to the product of the quantum yield: $\phi$ and the sum of charge-carrier mobilities: $\mu \Sigma = \mu_{\phi} + \mu_{M}$, by $\phi \Sigma \Delta \sigma = \Delta \phi_{\Sigma}(\Sigma \Delta \sigma)$, where $\phi$, $\mu$ and $\Delta \sigma$ are the unit charge of a single electron (in C), incident photon density of excitation laser (in m$^{-2}$) and a correction (or filling) factor (in m$^{-3}$), respectively. $\Delta \phi_{\Sigma}$ was calculated by taking into consideration the geometry and optical properties of the sample such as the size, laser cross-section and absorption of the excitation laser.

**Samples for optical measurements.** Thin solvent-free liquid pastes were prepared using spatula on a quartz substrate for the fluorescence and optical absorption measurements.

**Preparation of liquid composites.** Finely powdered dopants (D1 and D2) were added to the solid anthracene (I) in the required molar ratio in a watch glass and blended using a spatula. Mixing of the components for around 1 min yielded the liquid composites as a yellow/orange pasty liquid, depending on the molar ratio of the dopant. The resulting composites were optically characterized by absorption and fluorescence spectroscopies.

**Samples for photo-stability NMR experiments.** The $^1$H and $^{13}$C NMR measurements were carried out after irradiation of 5 and 20 mg of compounds per 1 g $\mathrm{CDCl}_3$ in the NMR tube. The irradiation time was optimized to be 14 h (I), 2 h (4) for $^1$H and 100 h (1, 4) for $^{13}$C NMR experiments.

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Author contributions
S.S.B. and T.N. designed the work, carried out research, analysed data and wrote the paper. J.A. and H.O. helped to characterize the molecules. M.J.H. contributed to small-angle X-ray scattering and NMR analysis. A.S. and S.S. performed the time-resolved microwave conductivity studies and fluorescence lifetime experiments. K.K., K.H., M.Y. and H.M. were involved in the work discussion and T.N. is the principal investigator. All authors discussed the results and commented on the manuscript.