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Introduction

Organic solid luminescent materials are being widely investigated for their potential applications in optoelectronic and biological fields, such as organic light-emitting diodes (OLEDs),¹ bioimaging,² chemo/biosensors,³ DSSCs⁴ and so on. Moreover, some organic materials can perceive changes in the surrounding environment, and make corresponding responses through dynamic and reversible fluorescence and color conversion. Among these luminogens, mechanofluorochromic (MFC) materials, the emissions of which can be repeatedly switched between different colors under external force stimuli such as grinding, pressing, shearing, smearing, or crushing, have received considerable attention in the construction of mechanical sensors, memory devices, security printing, data-storage devices, optical displays, and so forth.^{5,6}

As is well known, conventional luminogens are normally highly emissive in dilute solutions while being weakly luminescent or even totally quenched when aggregated, demonstrating aggregation-caused quenching (ACQ) behavior, which limits

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Remarkable isomeric effects on the mechanofluorochromism of tetraphenylethylene-based $D-\pi-A$ derivatives[†]

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Three tetraphenylethylene (TPE) decorated benzaldehyde isomers were designed and synthesized *via* the Suzuki–Miyaura coupling reaction with higher yields by changing the linking positions of the peripheral TPE units to demonstrate the isomeric effects on the photophysical and MFC properties. The changes of the linking positions could alter the molecular packing modes, and thus, their solid-state fluorescence properties exhibit remarkable isomeric effects. Interestingly, the three isomers are all aggregation induced emission (AIE) and MFC dyes. And the MFC activities of the three compounds are increased with the sequence of *m*-TPEC (45 nm) > *p*-TPEC (39 nm) > *o*-TPEC (8 nm). X-ray structural analysis, XRD, DSC and theoretical studies suggest that the change from a crystalline phase with a twisted molecular structure to a more planar amorphous phase should be responsible for the MFC properties. These findings suggest that subtle manipulation of the end groups capped at benzaldehyde could significantly alter and tune the photophysical properties. And these results will be of great help in understanding the structure–property relationships of MFC mechanisms and designing more new MFC materials.

their applications. This situation was greatly improved by the important discovery of the aggregation induced emission (AIE) phenomenon by Tang et al. in 2001.⁷ The luminogens with the AIE feature usually show strong fluorescence upon aggregation, which is beneficial for the acquisition of high-contrast mechanochromic luminescent materials. Recently, a lot of organic fluorescent small molecules have been designed to simultaneously exhibit AIE and MFC properties.8 However, to date, organic luminescent small molecules exhibiting mechanofluorochromic characteristics with AIE are still insufficient, and designing and synthesizing such compounds containing the two properties is meaningful and challenging. It is common knowledge that solidstate optical properties strongly depend on molecular packing arrangements, so controlling the molecular packing could be a promising strategy via chemical or physical alterations to tune the solid state fluorescence properties.9 Moreover, modification of existing chromophores is an interesting and easy way to regulate the solid state emission, because of the known synthetic pathway and expected photophysical characteristics. In recent years, positional isomers and polymorph dependent modulated emissions have been wielded for various applications.¹⁰ Therefore, further understanding the relationships between fluorescence properties and molecular packing/conformation of positional isomers could be more interesting and would be key for future application of the designed fluorophores. More and more extended conjugated systems, and donor-acceptor (D-A) and donor- π -acceptor (D- π -A) chromophores have been



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Scheme 1 Synthetic routes of o-TPEC, m-TPEC, and p-TPEC.

found to show optical properties *via* changing the position of the substituents.¹⁰

Above all, deciphering the structure-property relationships of AIE luminogens is crucial to further molecular design and understand the mechanism of operation. In this contribution, we designed and synthesized three TPE-decorated benzaldehyde isomers in high yields (Scheme 1) aiming to indicate the effect of the substitution position on MFC. Then, we investigated the aggregation-induced emission (AIE) properties in THF-H₂O mixtures and reversible mechanochromic luminescent properties by grinding with a mortar and pestle and fuming with dichloromethane (DCM). Interestingly, the three isomers showed different MFC properties. X-ray structural analysis, XRD, DSC and theoretical studies were performed to gain more insight on the fluorescence switching mechanism. These studies suggest that the switching of fluorescence was due to the change from the crystalline phase with a twisted molecular structure to a more planar amorphous phase.

Results and discussion

The target compounds were prepared in moderate to high yields (78–85%) by Suzuki–Miyaura cross-coupling reactions catalyzed by the palladium(0) complex, as illustrated in Scheme 1. Briefly, *p*-TPEC was obtained by the coupling between (2-(4bromophenyl)ethene-1,1,2-triyl)tribenzene and (4-formylphenyl)boronic acid, while the other compounds were prepared by the coupling between (2-(4-bromophenyl)ethene-1,1,2-triyl)tribenzene and the corresponding boronic acids. The resulting compounds were characterized by NMR spectroscopy and elemental analysis, with satisfactory results being obtained.

Aggregation induced emission investigation

The absorption and fluorescence spectra of the three isomers in THF (10^{-5} M) are given in Fig. S1 (ESI[†]). The absorption peaks/ shoulders at 247/300/325, 247/324, and 247/295/342 nm are recorded for *o*-TPEC, *m*-TPEC, and *p*-TPEC, respectively. The last band is assignable to the intramolecular charge transfer (ICT) transition. And the fluorescence emission peaks are measured at 424, 408, and 483 nm for *o*-TPEC, *m*-TPEC, and *p*-TPEC, respectively. These results indicate that *p*-TPEC has the largest conjugation among the three isomers.

Upon UV irradiation, the THF solutions of the three isomers are weakly or even nonemissive, which should be ascribed to the highly active energy consuming intramolecular motions.



Fig. 1 Images of **o-TPEC**, **m-TPEC**, and **p-TPEC** in THF solution $(10^{-5} \text{ M}, \text{top})$ and the solid state (bottom) under 365 nm light.

However, their solids exhibited strong fluorescence under 365 nm light (Fig. 1). This result suggests that the three compounds may be AIE molecules. This is further proved by a solventnonsolvent fluorescence test. o-TPEC, m-TPEC, and p-TPEC are highly soluble in THF, but insoluble in water. Using THF/water as a mixed solvent and increasing the water fraction would cause these molecules to aggregate and change their emission spectra. As shown in Fig. 2, the fluorescence peak intensities of p-TPEC are gradually intensified with the growing water fraction. It was understandable that a new emission peak (shoulder) appeared at about 500 nm for *p***-TPEC** in THF/H₂O with $f_w \ge 20\%$ with the emission intensities gradually intensified. And when the water fraction was at 90%, the fluorescence intensity of the mixture solution reached the maximum with about 3.5-fold enhancement higher than that in THF ($f_w = 0\%$). The fluorescence intensity increased significantly with the water fraction below 50% for compound o-TPEC. However, when the water fraction was at 60%, the fluorescence intensity of the mixture solution reached the maximum with a 2.82-fold enhancement higher than that in pure THF. However the FL intensity decreased with the water fraction over 60%, and when the water fraction was 80%, the fluorescence intensity was near to that of the THF solution. The fluorescence behavior of *m*-TPEC in THF/H₂O solution was similar to that of o-TPEC (Fig. S2, ESI[†]). The strong emission of o-TPEC ($f_w = 0.5$), m-TPEC ($f_w = 0.6$) and p-TPEC $(f_w = 0.9)$ can be attributed to the formation of aggregates. The aggregate formation was confirmed by field emission scanning electron microscopy (FESEM) measurements (Fig. S3, ESI⁺). The UV-vis absorption spectra of o-TPEC, m-TPEC, and p-TPEC were obtained in THF/water mixtures (Fig. S4, ESI[†]), and a level-off tail started to appear in the longer wavelength region when the water content exceeded 50% (o-TPEC), 40% (m-TPEC) and



Fig. 2 Fluorescence spectra of *p*-TPEC in the mixtures of THF and water with different volume ratios (a); the plots of the intensities vs. water content (b); the inset is the corresponding images of *p*-TPEC under 365 nm light.

50% (*p*-TPEC), respectively, confirming the formation of aggregates.¹¹ To quantitatively estimate the emission properties, the PL efficiencies of the luminogens in THF solution (Φ_{fss}) and asprepared solid (Φ_{fsolid}) states were determined. The Φ_{fss} values are as low as 0.61%, 0.86%, and 0.78% for *o*-TPEC, *m*-TPEC, and *p*-TPEC, and their Φ_{fsolid} values are boosted to 8.8%, 24.4%, and 22.8%, yielding AIE factors ($\alpha_{AIE} = \Phi_{fsolid}/\Phi_{fs}$) of 14.4, 28.4, and 29.3, respectively.^{6c} The relatively low Φ_{fsolid} of *o*-TPEC might be ascribed to its more active molecular motions in the solid state.^{9b} As mentioned above, the three isomers should be AIE molecules.

Electrochemical properties and density functional theory calculations

To more deeply study the three AIE molecules at the molecular level, quantum mechanical computations were carried out to obtain the optimized geometry of the compounds. The lowest energy spatial conformations were calculated using Gaussian 09W software. Fig. 4 shows the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of o-TPEC, m-TPEC, and p-TPEC after structural optimization by the density functional method at the B3LYP/6-31G(d,p) level. The optimized geometries show twisted conformations with different dihedral angles of the TPE group and the adjacent phenyl group, which are calculated to be 130.75°, 34.92° and 34.63° (Fig. S5, ESI[†]), respectively, which indicated that they are non-planar molecules. Interestingly, obvious migrations of electron clouds are discovered from the TPE groups to the formyl groups, and little difference in the migration of the electron clouds among these compounds was found (Fig. 3). As little difference in the migration of the electron clouds was found, we further carried out quantitative analysis of the electronic spectral data to explore the divergence between the dipole moment and the energy gap. As shown in Table 1, timedependent density functional theory (TD-DFT) calculations were carried out, and the dipole moments of the compounds were determined to be 3.78, 3.63, and 4.83 Debye for o-TPEC, *m*-TPEC, and *p*-TPEC respectively, which indicated that *p*-TPEC had the largest molecular polarity. The calculated energy gaps according to the difference in the HOMO and the LUMO for o-TPEC, m-TPEC, and p-TPEC were 3.61, 3.51 and 3.44 eV,



Fig. 3 Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of *o*-TPEC, *m*-TPEC, and *p*-TPEC.



Fig. 4 Photos of **o-TPEC**, **m-TPEC** and **p-TPEC** color changes under grinding and furning or heating stimuli conditions using a 365 nm UV lamp.

Table 1 Electronic spectral data of **o-TPEC**, **m-TPEC**, and **p-TPEC** calculated with TD-DFT at the B3LYP/6-31 G level

Compound	f^{a}	μ^b (debye)	HOMO (eV)	LUMO (eV)	HOMO ^c (eV)	E_1^d (eV)	E_2^e (eV)
o-TPEC	0.1265	3.78	-5.44	-1.83	-5.01	3.61	3.15
<i>m</i> -TPEC	0.0289	3.63	-5.38	-1.87	-5.05	3.51	3.24
<i>p</i> -TPEC	0.3977	4.83	-5.46	-2.02	-5.09	3.44	3.14

^{*a*} Oscillator strength. ^{*b*} Dipole moment. ^{*c*} Obtained using the onset oxidation potentials from CV curves. ^{*d*} Energy gaps calculated from quantum chemical analysis. ^{*e*} Energy gaps calculated from UV-vis absorption spectra.

respectively. The energy levels of the HOMOs were also obtained using the onset oxidation potentials from the CV curves (Fig. S6, ESI†), and were consistent with the result of quantum chemical computations. At the same time, the energy gaps calculated from the UV-vis absorption spectra for *o*-TPEC, *m*-TPEC, and *p*-TPEC were about 3.15, 3.24, and 3.14 eV, respectively. Moreover, the stimulated absorption spectrum showed strong absorption bands with maxima of *ca.* 392.4 nm, 393.3 nm and 399.9 nm because of the transition from the HOMO to the LUMO (Fig. S7–S9 and Tables S1–S3, ESI†).

Mechanofluorochromism (MFC)

As is well known, some AIE materials with a twisted structure possess MFC properties. From the DFT analysis of o-TPEC, *m*-TPEC, and *p*-TPEC, the structures possessed big torsions. Thus, to check whether the three isomers possess MFC properties, a small amount of the pristine powers was ground using vegetable parchments, and under UV irradiation a greenishyellow letter "T", yellowish-green letter "P", and bright-yellow letter "E" were seen clearly on the "paper" in the written area for o-TPEC, m-TPEC, and p-TPEC, and their emitting colors changed into blue-green, bright blue, and cyan light upon fuming by DCM for about 30 s (for o-TPEC) or 90 s (for m-TPEC and p-TPEC). Moreover, the fluorescence color could also be restored to that of the pristine material by heating the ground powder for 10 min at 110 °C (Fig. 4). In order to gain further information, the emission spectra of o-TPEC, m-TPEC, and p-TPEC in solid states were investigated. As shown in Fig. 5, the as-prepared solids of o-TPEC, m-TPEC, and p-TPEC showed emission peaks/shoulders at 488/498, 470, and 483 nm, respectively, whereas their ground



Fig. 5 Normalized PL spectra of **o-TPEC** ($\lambda_{ex} = 420$ nm), **m-TPEC** ($\lambda_{ex} = 400$ nm), and **p-TPEC** ($\lambda_{ex} = 425$ nm) in different solid-states: pristine, grinding, heating and fuming.

amorphous solids exhibit greenish yellow or yellow emissions with maxima at about 506, 515, and 522 nm. The grindinginduced spectral shifts for *o*-TPEC, *m*-TPEC, and *p*-TPEC were about 8 nm, 45 nm, and 39 nm. And the MFC activities of the three compounds increased with the sequence of *m*-TPEC > *p*-TPEC > *o*-TPEC. The solid fluorescence efficiencies (Φ) of the ground *o*-TPEC, *m*-TPEC, and *p*-TPEC solids are 9.3%, 21.2%, and 20.4%, respectively, which are lower than those of the crystalline states except for *o*-TPEC. After being fumed with dichloromethane (DCM) solvent, the emissions of the ground solids can be restored to their original states, thus suggesting the reversibility of the mechanochromism. Moreover, this reversible change of emissive color can be repeated many times without fatigue under alternating grinding and solvent fuming procedures (Fig. S10, ESI†).

In most cases, the mechanism of the MFC behavior results from the change of molecular packing modes upon external force. To deeply understand what happens upon pressing the three isomers, powder wide-angle X-ray diffraction (XRD) and differential scanning calorimetry (DSC) experiments were conducted using the original, ground, and fumed samples. As shown in Fig. 6, the sharp scattering and intense peaks in the original solids suggested well-ordered microcrystalline structures. In contrast, the diffraction patterns of the ground samples showed decreased or even no diffraction peaks, indicating that the microcrystalline structure was destroyed and transformed to an amorphous structure.^{12,13} As expected, the fumed samples led to the regeneration of well-ordered microcrystalline structures accompanying the reappearance of sharp scattering peaks, which was consistent with the original samples and implied the restoration of the original regular crystalline molecular packing. The results indicated that the phase transition between the crystalline and amorphous states would cause MFC behaviours. It is also noteworthy that, the crystalline fluorescence emission is blue-shifted compared to its amorphous one, which indicated that the molecular conformation is more twisted in the crystalline than amorphous states.^{9b} In addition, DSC thermograms of



Fig. 6 Powder wide-angle X-ray diffraction patterns of **o-TPEC**, **m-TPEC**, and **p-TPEC** in different states at room temperature.



Fig. 7 DSC curves of **o-TPEC**, **m-TPEC**, and **p-TPEC** under pristine and ground states.

pristine and ground samples showed that new exothermal re-crystallization peaks were observed at 102.7 °C, 93.8 °C, and 98.2 °C for ground *o*-TPEC, *m*-TPEC, and *p*-TPEC samples, respectively (Fig. 7). These results indicated that at the abovementioned temperatures, thermal re-crystallization begins for these ground amorphous powders, and it can be concluded that the crystals of pristine samples were destroyed and converted to the amorphous state by the grinding treatment.^{5,9}

Fortunately, we are able to obtain a single crystal of *o*-TPEC suitable for crystal structure analysis, and the single crystal X-ray structure of *o*-TPEC provides more insight into the mechanochromic behaviors. As shown in Fig. 8 *o*-TPEC adopts twisted conformations, one *o*-TPEC molecule has three intermolecular



Fig. 8 Molecular packing of **o-TPEC** in single crystals with C–H···O (2.70 Å) and C–H··· π (2.88, 2.90 Å).

weak interactions with four other molecules, including C-H···O (2.70 Å) and C-H··· π (2.88 Å and 2.90 Å). Such twisted conformations not only facilitate intramolecular motions in solution, which can effectively consume the exciton energies, thus making it poorly emissive, but also suppress the π - π staking of the molecules in crystals. Meanwhile, intermolecular interactions firmly rigidify the molecular conformations, thus diminishing nonradiative deactivation of the excitons. Moreover, such twisted conformations in crystals are easy to planarize upon grinding, thus generating red-shifted emission.^{9b}

Conclusions

Three TPE decorated benzaldehyde isomers were designed and synthesized via the Suzuki-Miyaura coupling reaction with higher yields. Interestingly, the three isomers are all aggregation induced emission (AIE) and MFC dyes. The solid emission studies showed that their fluorescence color could change reversibly between blue-green, (488/498 nm), bright blue (470 nm), and cyan (483 nm), and greenish-yellow (506 nm), yellowish-green (515 nm), and bright-yellow (522 nm) through grinding and dichloromethane (DCM) fuming treatment, giving large spectral red-shifts of 8, 45, and 39 nm, respectively. And the MFC activities of the three compounds are increased with the sequence of *m*-TPEC (45 nm) > p-TPEC (39 nm) > o-TPEC (8 nm). X-ray structural analysis, XRD, DSC and theoretical studies suggest that the change from the crystalline phase with a twisted molecular structure to a more planar amorphous phase should be responsible for the MFC properties. These results suggest the potential applications of these luminogens as smart mechanochromic materials.

Experimental section

Measurements and instruments

All the raw materials were used without further purification. All the solvents were purchased from Beijing Chemical Works (Beijing, China) and were of analytical reagent grade; moreover, they were used without further purification. The ¹H NMR and ¹³C NMR spectra were recorded using a Mercury Plus instrument at 600 MHz and 151 MHz by using CDCl₃ as the solvent in all cases. The HR-MS spectra were recorded using a Bruker Impact II. The UV-vis absorption spectra were obtained using a VARIAN Cary 5000 spectrophotometer. The absorption spectra of the solids were obtained by measuring their films on the surface of a silica plate. Photoluminescence measurements were obtained using a Cary Eclipse fluorescence spectrophotometer. The fluorescence quantum yields of TPE-based derivatives in solvents were measured by comparing with a standard (quinine in 0.1 N H₂SO₄, $\Phi_{\rm F}$ = 0.546) and the excitation wavelength was 365 nm. C, H, and N elemental analyses were performed using a vario MACRO cube elemental analyzer. The XRD patterns were obtained using an Empyrean X-ray diffraction instrument equipped with graphite-monochromatized Cu Ka radiation (λ = 1.5418 Å) by employing a scanning rate of $0.026^{\circ} \text{ s}^{-1}$ in the 2θ range from 5 to 50. Differential scanning calorimetry (DSC) curves were obtained using a DSC 200 F3 at a heating rate of 10 °C min⁻¹, and the data of all samples (pristine and ground) were collected when they were heated for the first time. FESEM was performed using a JSM-7500F. The molecular configuration was used to obtain the frontier orbitals of *o*-TPEC, *m*-TPEC, and *p*-TPEC by density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) level with the Gaussian 09W program package. The single-crystal X-ray diffraction data of the *o*-TPEC crystal were collected using a Bruker D8 Venture diffractometer. The CCDC number of *o*-TPEC is 1853608.

Synthesis

4'-(1,2,2-Triphenylvinyl)-[1,1'-biphenyl]-2-carbaldehyde (o-TPEC). Under an atmosphere of nitrogen, to a mixture of compound (2-(4-bromophenyl)ethene-1,1,2-triyl)tribenzene (411 mg, 1.0 mmol), 2-(dihydroxyboryl)benzaldehyde (225 mg, 1.5 mmol) and Pd(PPh₃)₄ (0.05 eq.) in 10 mL toluene/H₂O (1:1) was added K₂CO₃ (345 mg, 2.5 mmol), and the reaction solution was refluxed overnight. The reaction mixture was cooled to room temperature and then poured into 500 mL water, extracted with CH2Cl2 and dried over anhydrous MgSO₄. The crude product was purified by column chromatography on silica gel (petroleum ether/DCM = 2/1) to yield o-TPEC as a white solid (349 mg, 80%). m.p.: 185-186 °C. IR (KBr, cm⁻¹): 758, 831, 1026, 1333, 1443, 1576, 2366, 2848, 3023, 3059, 3078. ¹H NMR (600 MHz, CDCl₃) δ = 9.89 (s, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 7.7 Hz, 1H), 7.15–7.11 (m, 13H), 7.10–7.07 (m, 3H), 7.07-7.04 (m, 3H) (Fig. S11, ESI[†]). ¹³C NMR (151 MHz, $CDCl_3$) $\delta = 192.54, 145.83, 143.85, 143.51, 143.44, 143.35,$ 141.83, 140.16, 135.56, 133.66, 133.50, 131.35, 131.30, 130.63, 129.48, 127.81, 127.74, 127.70, 127.64, 127.48, 126.75, 126.65, 126.61 (Fig. S12, ESI[†]). HR-MS: m/z 459.1713, $[M + Na]^{\dagger}$ (Fig. S13, ESI,[†] calcd for $C_{33}H_{24}$ ONa: 459.1719); anal. calcd (%) for C33H24O: C, 90.79; H, 5.54; N, 3.67. Found (%): C, 90.75; H, 5.55; N, 3.69.

4'-(1,2,2-Triphenylvinyl)-[1,1'-biphenyl]-3-carbaldehyde (m-TPEC). The synthetic method for compound *m*-TPEC was similar to that of compound o-TPEC. It was purified by column chromatography (silica gel, petroleum ether/ $CH_2Cl_2 = 1/1$) to afford a white solid (78% in yield). m.p.: 150–152 °C. IR (KBr, cm⁻¹): 766, 832, 1027, 1361, 1441, 1583, 1732, 2355, 2733, 3030, 3055, 3078. ¹H NMR (600 MHz, CDCl₃) δ = 10.06 (s, 1H), 8.05 (s, 1H), 7.81 (d, J = 7.7 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.38 (d, J = 8.3Hz, 2H), 7.14-7.09 (m, 11H), 7.09-7.06 (m, 4H), 7.05-7.03 (m, 2H) (Fig. S14, ESI[†]). ¹³C NMR (151 MHz, CDCl₃) ¹³C NMR (151 MHz, $CDCl_3$) δ = 192.38, 143.66, 143.62, 143.61, 143.57, 141.69, 141.51, 140.25, 137.35, 136.87, 132.80, 132.01, 131.39, 131.34, 131.33, 129.42, 129.02, 128.51, 127.98, 127.82, 127.76, 127.68, 126.63, 126.58, 126.53, 126.27 (Fig. S15, ESI⁺). HR-MS: m/z 459.1705, $[M + Na]^+$ (Fig. S16, ESI,[†] calcd for C₃₃H₂₄ONa: 459.1719); anal. calcd (%) for C₃₃H₂₄O: C, 90.79; H, 5.54; N, 3.67. Found (%): C, 90.75; H, 5.52; N, 3.69.

4'-(1,2,2-Triphenylvinyl)-[1,1'-biphenyl]-4-carbaldehyde (*p*-TPEC). The synthetic method for compound *p*-TPEC was similar to

that of compound **o**-**TPEC**. It was purified by column chromatography (silica gel, petroleum ether/CH₂Cl₂ = 1/1) to give a white solid (85% in yield). m.p.: 196–198 °C. IR (KBr, cm⁻¹): 765, 821, 1025, 1308, 1444, 1696, 1726, 2343, 2725, 2821, 3030, 3056, 3075. ¹H NMR (600 MHz, CDCl₃) δ = 10.03 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.14–7.10 (m, 11H), 7.09–7.05 (m, 4H), 7.05–7.02 (m, 2H) (Fig. S17, ESI†). ¹³C NMR (151 MHz, CDCl₃) δ = 191.92, 146.69, 144.22, 143.56, 143.51, 141.68, 140.17, 137.29, 135.05, 132.03, 131.39, 131.34, 131.31, 130.23, 127.83, 127.78, 127.68, 127.37, 126.66, 126.61, 126.57, 126.53 (Fig. S18, ESI†). HR-MS: *m*/*z* 459.1703, [M + Na]⁺ (Fig. S19, ESI,† calcd for C₃₃H₂₄ONa: 459.1719); anal. calcd (%) for C₃₃H₂₄O: C, 90.79; H, 5.54; N, 3.67. Found (%): C, 90.75; H, 5.54; N, 3.69.

Conflicts of interest

There are no conflicts to declare.

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