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Introduction

Stimuli-responsive materials are receiving increasing attention in terms of academic importance and practical application, especially organic chromophores whose emission or colour can be tuned by various external stimuli.1 Nowadays compounds with mechano-thermo-vapochromic,² mechano-photochromic,³ photo-electrochromic,4 electro-acidochromic5 or mechanoacidochromic6 properties are being developed. However, mechano-electrochromic materials, which synchronously possess force and electric dependent optical properties, have rarely been reported due to the lack of molecular design principles. As electrical power is indispensable to the modern world, and mechanical stimulation can be carried out simply with hands, the mechano-electrochromic chromophores can find significant and captivating potential applications in touch screens, biosensors and optoelectronic devices, especially the displays whose input information can be supplied as both a sophisticated electrical signal and an *in situ* manual drawing.

As for mechanochromic (MC) properties, meaning that the emission can be reversibly transformed through altering of molecular packing structures upon grinding, shearing or

State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, College of Chemical Engineering and Materials Science, Zhejiang University of Technology, HangZhou, P. R. China. E-mail: czhang@zjut.edu.cn; ouyang@zjut.edu.cn † Electronic supplementary information (ESI) available. See DOI: 10.1039/c4tc00516c

A donor-acceptor cruciform π -system: high contrast mechanochromic properties and multicolour electrochromic behavior[†]

Jingwei Sun, Xiaojing Lv, Pingjing Wang, Yujian Zhang, Yuyu Dai, Qichao Wu, Mi Ouyang* and Cheng Zhang*

A donor-acceptor (D–A) cruciform conjugated luminophore DMCS-TPA was designed and synthesized. The DMCS-TPA solid shows both aggregation induced emission (AIE) effect and high contrast mechanochromic (MC) behavior with a remarkable spectral shift of 87 nm. The obvious fluorescence switching from yellowish green to orange can be realized by pressing at only 10 MPa or simply grinding. The photophysical properties, theory calculation and XPS results demonstrate that the extension of the conjugation length and subsequent enhancement of intramolecular charge transfer (ICT) transition are responsible for the improved MC performance. In addition, DMCS-TPA is readily deposited on the ITO electrode surface by the electrochemical method to form an electrochromic (EC) film with multiple colours showing (light green at 0 V, red at 1 V, grey at 1.1 V and blue at 1.45 V) and a high optical contrast of 65% at 769 nm. The results suggest that incorporation of electroactive moieties into luminophores to constitute D–A cruciform conjugated structures is a promising design strategy for preparing dual functional materials combining MC and EC properties.

pressing, one of the recent goals for practical applications is improving the contrast ratio in emission intensity or wavelength. Several fluorescent on-off switching materials with high contrast have been reported.7 However examples with a broad colour change are rather scarce at the current stage⁸ due to the complicated requirements of both remarkable shift of PL wavelength and high solid-state emission efficiency. Tian's group obtained divinylanthracene derivatives showing more than 100 nm red-shift under high pressure, for example, above one GPa,9 but relatively low pressure is preferred for applications in our daily life. Therefore, development of new AIE-active luminogens with large emission wavelength change under moderate pressure is strikingly desirable. As for electrochromism, that the colour can be reversibly modulated by applying electrochemical potential, the construction of monomers having multiple redox states with different absorptions is fairly important for preparation of multicolour electrochromic materials.10 Besides, to achieve dual response characteristic (such as MC and EC), the key design concept is incorporating corresponding functional units in a single molecule, while along with it is the ambiguous intramolecular and intermolecular interference influencing the band-gap and excitonic coupling and thus the photophysical performance of the material. As such, outlining the molecular design principles is a great challenge for preparing efficient mechano-electrochromic materials.

The donor-acceptor cruciform π -system, which is characterized by rigid X-shaped geometry with donors and acceptors

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respectively on two crossed axes, has been explored widely in chemical sensors, non-linear optical devices, OLEDs, OFETs and molecular electronics owing to its unique electronic and optical properties as well as aggregate structures.11 Herein, for the design of organic chromophores that respond to both mechanic and electric stimuli, we present the electron D-A cruciform conjugation strategy via adopting triphenylamine (TPA) donors suspended on both sides of the central phenyl of the dicyanodistyrylbenzene (DCS) moiety. This approach has the following advantages. First, the cruciform structure can successfully incorporate units with different functions into each branch, for instance, one bar provides the electroactive species (TPA) while the other serves as the luminogen (DCS). Second, the crowding in the central part forces the surrounding substituents to distort from the ring plane, resulting in effective depression of close packing and enhancement of emission quantum yields in the solid state.12 Finally, it has been demonstrated that a large bathochromic shift of fluorescence can be expected from mechanochromic dyes with push-pull features owing to their strong dipole-dipole interactions.¹³ In particular, the D-A cruciform conjugations generally show spatially separated frontier molecular orbitals (FMOs) with a vanishingly small overlap in the central core between the HOMO and LUMO.11e-g The extraordinary HOMO and LUMO located on crossed directions respectively might induce intriguing optical and electronic properties.

In this work, we designed and synthesised an interesting novel model compound DMCS-TPA (Scheme 1). For comparison, the linear molecule BMBCP without TPA donors was prepared and characterized. DMCS-TPA exhibits MC properties with a remarkable emission peak shift of 87 nm and fluorescent efficiencies of 48.59% and 34.53% before and after grinding, much higher than those of BMBCP. The obvious fluorescence (colour) transition from yellowish green (yellow) to orange (orange) can be realized by simply grinding or pressing at only 10 MPa. In addition, DMCS-TPA is readily deposited on the ITO



Scheme 1 Synthesis route to DMCS-TPA and BMBCP. (a) (4-(Diphenylamino) phenyl)boronic acid, Pd(PPh₃)₄, Na₂CO₃ (aq), toluene/THF, reflux; (b) 2-(3-methoxyphenyl)acetonitrile, NaOCH₃, chromatographic grade ethanol, r.t.

electrode surface by the electrochemical method to form an electrochromic film with multiple colours showing (light green, red, grey and blue). A systematic study of the photophysical properties, structure characteristics and theoretical calculations has been carried out to examine the reasonable molecular design strategy.

Results and discussion

Photophysical properties

The optical properties of DMCS-TPA in solvents of varying polarities were investigated by UV-vis absorption and PL spectroscopy. For comparison, the absorption and emission spectra of BMBCP in dilute solution are shown in Fig. 1. DMCS-TPA exhibits two prominent emission bands: one with a vibrational structure that remains located at around 430 nm and the other significantly shifts from 513 nm to 595 nm with the solvent changing from hexane to chloroform. The blue region emissions of DMCS-TPA, which are similar in different solvents, might originate from the DCS moiety because of their analogous spectra with those of BMBCP in the monomer state. The hypochromatic peaks of about 21 nm relative to those of BMBCP are attributed to the twisted molecular conformation and decreased conjugation induced by the steric hindrances. The longer wavelength emissions can be assigned to the intramolecular charge transfer (ICT) effect due to the large solvatochromism with increasing solvent polarity. In addition, the quantum yields ($\phi_{\rm F}$) of DMCS-TPA in solution decrease from 6.9% (toluene) to 5.0% (chloroform) and less than 0.01% (DMF). The excitation spectra monitored at both emission maxima are shown in Fig. S1.[†] Particularly, when monitored at 430 nm, DMCS-TPA molecules exhibit excitation profiles almost mirror symmetric with the emission spectra. For BMBCP, no obvious ICT emission was observed in solutions. The results imply that an obvious charge transfer from the TPA axis to the DCS axis takes place in excited DMCS-TPA. Unlike the case of emission, the absorption spectra of DMCS-TPA are almost identical irrespective of the kinds of solvents, showing the main band at 349 nm together with a much weaker shoulder at around 438 nm. The shoulder peak, which is apparently absent



Fig. 1 Normalized absorption and photoluminescence (PL) spectra of DMCS-TPA in (a) hexane, (b) toluene, (c) chloroform and (d) BMBCP in toluene.

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in BMBCP, is ascribed to the ICT transition. On one hand, the congested central part where bulky substituents suspend surround the benzene core leads to largely twisted molecular conformation with shortened conjugation, which might result in a blue-shift tendency; on the other hand, the electron-rich TPA units together with the electron-withdrawing –CN induce the ICT effect in the excited state and give rise to red-shifted emission depending on the solvent polarity. The joint effect between the conjugation and ICT degree defines the emission of DMCS-TPA.

The dual emission observed for DMCS-TPA in solution is unusual and intriguing. Further studies on excitation wavelength dependent emission have been conducted. Fig. 2 shows the PL spectra of DMCS-TPA in hexane with excitation wavelength increasing from 310 nm to 390 nm. Different from linear D-A molecules,^{14a} the higher energy emission keeps intensifying, while the ICT emission enhances with excitation wavelength changing from 310 nm to 350 nm, then gradually weakens and even vanishes when excitation increases to 390 nm. A similar phenomenon was observed for DMCS-TPA in toluene and chloroform solutions (Fig. S2 and S3[†]). These results are consistent with the excitation profiles in Fig. S1.[†] The special wavelength dependent emission, together with the dual emission feature, implies a large gap between the local excited (LE) and ICT energy level and a very slow internal conversion between the two states, which leads the LE to dominate the luminescence when excited at the lower energy region.

To elucidate the influence of the geometric and electronic structure of DMCS-TPA on photophysical properties, we conducted theoretical calculations. The DFT calculations were performed *via* Gaussian 09 at the B3LYP/6-31 G (d) level. As shown in Fig. 3, compared with BMBCP, DMCS-TPA shows a specially twisted conformation. The dihedral angles between two side benzene rings and the central core are 44.4° and 47.9°, respectively. And the dihedral angles between two vinyl planes and the central benzene are 28.7° and 28.8° respectively, much larger than those in BMBCP (5.5° and 5.2°). Such high torsional angles in DMCS-TPA would inhibit close packing and π - π interactions in the condensed state, leading to an emissive organic solid. In addition, it is intriguing to note that the



Fig. 2 Dependence of emission spectra as a function of excitation wavelength for DMCS-TPA in hexane solution.

Table 1 Optical properties of DMCS-TPA and BMBCP in the solid state

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Samples	$\lambda_{em} (nm)$	$\phi_{\mathrm{F}}\left(\% ight)$	τ_1 (ns) (%)	τ_2 (ns) (%)	τ (ns)
DMCS-TPA powder	512	48.59	2.138 (56.08)	5.920 (43.92)	3.80
DMCS-TPA ground	599	34.53	2.147 (48.67)	10.040 (51.33)	6.20
BMBCP powder	500	42.35			9.83
BMBCP ground	555	22.48	6.785 (33.75)	19.316 (66.25)	15.09

HOMO for DMCS-TPA is concentrated predominantly on the TPA units and the central phenyl, while the LUMO rearranges along the –CN containing axis. The strong charge transfer from one TPA to the crossed axis further reveals its typical ICT nature. The bandgap of 2.58 eV is consistent with that estimated from the onset wavelength of absorption.

The AIE effect of DMCS-TPA was examined in THF-water mixtures via UV-vis absorption and PL spectra (Fig. S4 and S5†). The absorption spectra of DMCS-TPA are slightly affected with water fractions below 40%. When the water content increased to 50%, the maximum absorption dropped abruptly with a rise in the shoulder around 430 nm and the long tail region, indicating the formation of DMCS-TPA nano-aggregates. Meanwhile, the maximum absorption wavelength shows a minor red shift from 347 nm to around 355 nm, which might arise from the extended π -conjugation in aggregates. Correspondingly, the fluorescence strengthened dramatically above 50% of water addition. The PL intensity continuously enhanced with increasing water content to 80%, leading to resultant intensity more than 10 fold larger than that of pure THF solution. The $\phi_{\rm F}$ of DMCS-TPA in THF was estimated to be 5.3% using 9,10-diphenylanthracene (DPA) in ethanol ($\phi_{\rm F}=95\%$) as the standard.¹⁶ While the DMCS-TPA powder shows bright yellowish green fluorescence with a $\phi_{\rm F}$ of 48.59% (Table 1), indicating its efficient emission in the solid state. The phenomenon demonstrates the AIE nature of DMCS-TPA, which could be attributed to the restricted internal rotations and decreased solvent polarity effect14 when molecules precipitate. The comparatively larger $\phi_{\rm F}$ value of DMCS-TPA powder than that of BMBCP (42.35%) implies that the cruciform structure of DMCS-TPA effectively depresses strong π - π interactions between the DCS axis thus diminishing emission quenching.

Mechanochromic properties

The fluorescence responses of DMCS-TPA towards mechanical, thermal and solvent-fuming processes are illustrated in Fig. 4. The as-prepared powder switch from yellowish green ($\lambda_{em} = 512$ nm, $\phi_F = 48.59\%$) to orange ($\lambda_{em} = 599$ nm, $\phi_F = 34.53\%$) luminescence was accompanied by the colour change from yellow to orange upon grinding. As shown in Fig. 5a, the PL spectra of the initial powder are significantly red-shifted by 87 nm with the peak width (FWHM) broadened from 69 nm to 116 nm after grinding. The remarkable conversion of the maximum PL wavelength is among the best results reported currently,^{8,9,17}



Fig. 3 Optimized conformation of DMCS-TPA and BMBCP (above) and calculated spatial electron distributions of HOMO and LUMO (below) of DMCA-TPA.



Fig. 4 Photographs of DMCS-TPA under 365 nm UV light upon different treatments.

which is enough clear to be readily visualized by the naked eye. Attractively, it can be restored to its original fluorescence through either thermal annealing at 80 °C for 5 min or solvent fuming with DCM. The pressure dependent emission of DMCS-TPA was further examined. A progressive change of the shape and position of fluorescence spectra with increased pressure from 2 MPa to 10 MPa was observed. As shown in Fig. 5b, application of 2 MPa induces a slight widening on the tail with little change of maximum PL wavelength. The powder pressed at 5 MPa exhibits a red shifted fluorescence at 544 nm. Adoption of 10 MPa causes a noticeable emission change by 74 nm from yellowish green to orange. The wide coverage of emissive spectra under a small load of pressure reveals the sensitive feature of DMCS-TPA towards mechanical stimuli. Whereas the sample subjected to 10 MPa is not stable at room temperature, showing a partial recovery within seconds. The mechanochromism can be recycled many times with almost no deterioration, indicating its reversibility and durability.

In comparison, BMBCP shows PL spectra switching from 500 nm to 555 nm with the $\phi_{\rm F}$ dropping from 42.35% to 22.48% upon grinding (Table 1). It is worth noting that the change of emission maximum before and after grinding is increased by

32 nm accompanied by an increase of more than 12% of $\phi_{\rm F}$ after grinding for DMCS-TPA relative to BMBCP. In addition, for BMBCP, both original powder and ground samples yield much longer fluorescence lifetime, implying the strong π - π interactions and excimer formation between BMBCP molecules.

To understand the mechanism of mechanochromic behaviour, powder XRD patterns of DMCS-TPA before and after grinding were investigated. As revealed in Fig. S6,† the pristine powder shows several sharp and intense reflections accompanied by a broad and diffuse peak around 22°, indicating a mixed crystal and amorphous phase. The ground solid does not give any noticeable diffraction in the XRD profile, reflecting its amorphous feature. In most cases, the MC phenomenon is mainly attributed to the change of intermolecular interactions and molecular arrangement in the condensed state,^{1a} however the unusual large shift of chromism in this case seems to reside mostly in the D-A cruciform module for its lower degree of crystallinity. A proposed explanation for the enhanced MC properties is that the distorted molecules, especially the TPA donors with large torsion angles, are subjected to conformational change and rotate to a position more parallel to the coplanar under external pressure,7f leading to extended conjugation¹⁸ and subsequent planar intramolecular charge transfer (PICT).7d The ICT delocalization in DMCS-TPA molecules will be greatly strengthened, resulting in remarkable red-shift of emission and decrease of fluorescent intensity. This proposal is evidenced by the UV-vis absorption13c and XPS spectra of original and ground DMCS-TPA.

Absorption spectra of DMCS-TPA in the two forms are presented in Fig. 6a. It is obvious that the shoulder peak at 430 nm red shifts to about 460 nm, indicating the extension of π conjugation after grinding. As shown in Fig. 6(b), the high resolution core level carbon C(1s) spectra of DMCS-TPA exhibit two features both before and after grinding: the main peak at around 284.8 eV which can be deconvoluted into four distinct peaks (Fig. S7 and S8[†]), and a much smaller satellite peak at the higher energy side originated from π electrons delocalized over the aromatic system. Table S1[†] summarizes the BE positions and percentage contributions from each of the resolved XPS peaks, which are in fair agreement with the characteristic banding features19 and the ideal stoichiometry. After grinding, a gentle increase in the intensity of the signal at 284.8 eV and a narrowing on the high binding energy side of the C(1s) peak were clearly observed. Meanwhile, the shake-up satellite, seen



Fig. 5 Luminescence spectra of the DMCS-TPA solid upon different treatments.

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from the magnified spectra, intensified and shifted from 291.5 eV to 292.8 eV compared with the pristine sample. The differences imply a large electronic rearrangement in the ground sample. As the electron donating ability of arylamine enhances with the increasing conjugation degree,¹⁵ the direction of charge rearrangement is supposed to be from the N (in TPA) to adjacent C atoms, resulting in electron-rich characteristic of C and downward BE positions. The intensified shake-up satellite is attributed to the enhanced delocalization of the π electron associated with the stronger charge transfer transition after grinding.

Electrochromic properties

As TPA is electroactive, we investigated the electrochemical characteristics of DMCS-TPA, and observed the intriguing electrochromic behaviour from its homopolymer. DMCS-TPA can be successfully polymerized *via* electro-synthesis, which is an effective approach for preparing cross-linked films directly onto a conducting substrate. Fig. 7(a) shows the cycle voltammetry polymerization spectra of DMCS-TPA on the ITO electrode. The CV traces show two oxidation peaks at 0.96 and 1.32 V and corresponding reduction peaks at 0.86 V and 1.04 V, respectively. Under repeated scanning, the oxidation currents at 0.96 V gradually raised, suggesting the growth of the conducting polymer film. The slight increase in the peak potential is attributed to the increase of resistance as the film thickening. The surface morphology of the film prepared through constant potential polymerization is depicted in the inset of Fig. 7(a).

The polymerized film displays four typical colours as increasing applied voltage. Those are light green at 0 V, red at 1 V, grey at 1.1 V and blue at 1.45 V. To understand the electrochromic properties, electrode potential correlated UV-vis absorption spectra of the film polymerized at 1.35 V were recorded. As shown in Fig. 7(b), in the neutral state from 0 V to 0.8 V, the film exhibits a strong absorption band centred at 350 nm, which can be assigned to the π - π * transition of the polymer backbone. Upon increasing the voltage gradually to 1.45 V, the peak at 350 nm continuously weakened. When the voltage reached 0.9 V, a shoulder peak at 484 nm appeared and strengthened to the maximum at 1.0 V. Then the intensity of the shoulder peak decreased and finally vanished at potentials from 1.1 V to 1.45 V. Simultaneously a new absorption band at around 769 nm emerged and enhanced along with the increase of the applied potential. The formation of new peaks at 484 and



Fig. 6 (a) The absorption and (b) XPS spectra of DMCS-TPA before and after grinding, the inset shows the magnified image.



Fig. 7 Spectroelectrochemical spectra of the P (DMCS-TPA) film at constant voltages from 0 V to 1.45 V in ACN solution containing 0.1 M TBAP.

769 nm could be ascribed to the evolution of polaron and bipolaron bands (Fig. 7).

The EC switching behaviour of the electro-polymerized DMCS-TPA films was monitored at the maximum absorption (350 and 769 nm) in order to characterize their optical contrasts. Fig. S9† exhibits the optical contrasts of the film, which were carried out between 0 and 1.45 V with a residence time of 3 s. A particularly high optical contrast of 65% was observed at wavelength of 769 nm, and 21% at 350 nm. While after multiple cycles of potential change, the film showed gradually weakened optical contrast, indicating that its stability was not good. Work aimed at improving the stability and durability of the electrochromic film is underway in our lab.

Conclusions

In summary, a novel D–A cruciform π -system DMCS-TPA with electroactive TPA substituted on both sides of the DCS moiety was designed and synthesized. The photophysical properties and theory calculation imply that DMCS-TPA possesses a highly twisted conformation with ICT character. Owing to the special cross-conjugated structure, DMCS-TPA shows both AIE effect and high contrast mechanochromic behavior with a remarkable spectral shift of 87 nm. The solid emission can be changed from yellowish green to orange upon simply grinding or pressing at only 10 MPa. From the results of absorption and XP spectra, the conjugation extension and ICT enhancement are believed to be responsible for the improved MC performance compared with BMBCP. In addition, DMCS-TPA can be electrochemically

deposited directly on ITO and exhibit electrochromic properties with multicolours showing (light green at 0 V, red at 1 V, grey at 1.1 V and blue at 1.45 V) and a high optical contrast of 65% at 769 nm. As far as we know, this is the first report on functional materials with combined MC and EC properties. The results suggest that incorporation of electroactive moieties into luminophores to constitute D-A cruciform conjugated structures might be a promising molecular design strategy for preparing efficient mechano-electrochromic materials.

Experimental section

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Chemicals and instruments

1,4-Dibromo-2,5-dimethylbenzene, terephthalaldehyde, (4-(diphenylamino)phenyl)boronic acid and 2-(3-methoxyphenyl) acetonitrile were purchased from commercial sources and used without further purification. 2,5-Dibromoterephthalaldehyde was synthesized according to the literature procedure.20 All solvents and reagents (analytical grade) were used as received, unless otherwise claimed.

The ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE III 500 MHz instrument (Bruker, Switzerland) using chloroform-d (CDCl₃) as the solvent. Mass spectroscopy was carried out with a Thermo LCQ Fleet MS spectrometer. Elemental analyses were performed using the Thermo-Finnigan Flash EA-1112 (CE, Italy) instrument. The UV-vis absorption spectrum was recorded on a Perkin Elmer Lambda 35 spectrophotometer. Fluorescent measurements were recorded on a Perkin-Elmer LS-55 luminescence spectrophotometer. The fluorescence quantum yield $\phi_{\rm F}$ was determined using a calibrated integrating sphere. Fluorescence lifetime experiments were performed by using the time-correlated single-photon counting (PicoHarp 300 TCSPC) system with right-angle sample geometry. A picosecond diode laser (PDL 800-B) was used to excite the samples. The minimum pulse width is 50 ps. The detection system uses a photomultiplier tube from Picoquant (R3809U-50) with an instrument response time less than 250 ps. Powder X-ray diffraction (XRD) was performed on a X' Pert PRO, PANalytical, with Cu-Ka radiation operating at 40 kV and 40 mA. X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlK α radiation. The base pressure was about 3 \times 10⁻⁹ mbar. The binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon. Field-emission scanning electron microscopy (SEM) measurements were performed by using a Hitachi S-4800 scanning electron microscope (Hitachi, Japan). The electrochemical property measurement was performed in a three-compartment system on a CHI660C electrochemical analyser (CH Instruments, China).

Synthesis

Synthesis of 4,4"-bis(diphenylamino)-[1,1':4',1"-terphenyl]-2',5'-dicarbaldehyde (1). Under a nitrogen atmosphere, a mixture of (4-(diphenylamino)phenyl)boronic acid (1.74 g, 6 mmol), 2,5-dibromoterephthalaldehyde (0.58 g, 2 mmol), Pd(PPh₃)₄ (0.065 g, 0.06 mmol), Na₂CO₃ (2.0 M, 3.0 mL), and View Article Online

to the mixture. The organic portion was separated and washed with brine before drying over anhydrous MgSO₄. The solvent was evaporated off, and the solid residues were purified by column chromatography to afford 0.87 g of 1 with a yield of 70.1%. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 10.18(s, 2H); 8.11(s, 2H); 7.33(t, I = 7.5 Hz, 8H); 7.29(d, I = 8.5 Hz, 4H); 7.20 (d, I =7.5 Hz, 8H); 7.18(d, J = 9.0 Hz, 4H); 7.11 (t, J = 7.5 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 192.15; 148.82; 147.30; 143.87; 136.75; 130.95; 130.15; 129.52; 125.11; 123.74; 122.46.

Synthesis of DMCS-TPA. 2-(3-Methoxyphenyl) acetonitrile (0.23 g, 1.55 mmol) and 1 (0.80 g, 1.29 mmol) were dissolved in anhydrous ethanol (20 mL) in the presence of sodium methoxide (0.80 g, 1.50 mmol). The mixture was stirred at room temperature for 6 hours. The resulting precipitate was filtered and washed with methyl alcohol several times to afford 0.94 g of DMCS-TPA with a yield of 82.9%. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.26 (s, 2H); 7.66 (s, 2H); 7.37 (d, J = 8.5 Hz, 4H); 7.34 (s, 2H); 7.31 (t, J = 7.5 Hz, 8H); 7.21 (d, J = 7.0 Hz, 4H); 7.19 (d, J = 8.0 Hz, 8H); 7.17 (d, J = 8.5 Hz, 4H); 7.09 (t, J = 7.5 Hz, 4H); 6.95 (dd, J = 8.5 Hz, 2H); 3.86 (s, 6H).¹³C NMR (125 MHz, CDCl₃): δ (ppm) 206.89, 160.14, 148.08, 147.34, 141.95, 140.88, 135.43, 131.15, 130.95, 130.25, 129.44, 125.04, 123.55, 122.44, 118.61, 114.96, 113.29, 111.69, 55.44, 53.43, 30.93. MS m/z: 878.4 (M+). Anal. calcd (%) for C₆₂H₄₆N₄O₂: C, 84.71; H, 5.27; N, 6.37; O, 3.64. Found: C, 85.15; H, 5.14; N, 6.21; O, 3.49.

Synthesis of BMBCP. The procedure is similar to that described for the synthesis of DMCS-TPA. ¹H NMR (500 MHz, $CDCl_3$: δ (ppm) 8.01 (s, 4H); 7.57 (s, 2H); 7.40 (t, J = 8.0 Hz, 2H); 7.31 (d, J = 7.5 Hz 2H); 7.23 (s, 2H); 6.98 (dd, J = 8.5 Hz, 2H); 3.90 (s, 6H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 160.19, 140.88, 135.62, 135.46, 130.21, 129.82, 118.56, 117.57, 115.24, 112.96, 111.78, 55.49. MS m/z: 392.3 (M+). Anal. calcd (%) for C₂₆H₂₀N₂O₂: C, 79.57; H, 5.14; N, 7.14; O, 8.15. Found: C, 79.65; H, 5.17; N, 7.01; O, 8.17.

Quantum chemical calculations

Single molecule calculations including optimized geometry, FMOs and dipolar moment in the ground state were performed at the density functional theory (DFT) level with B3LYP functional and 6-31G* basis set using the Gaussian 09 software.

Electrochemistry

Electrochemical polymerization and measurements were performed in a conventional three-electrode cell with an ITOcoated glass as the working electrode which was sequently washed with deionized water, ethanol and acetone under ultrasonication before use, a platinum (Pt) sheet and a doublejunction Ag/AgCl electrode (silver wire coated with AgCl in saturated KCl solution) were applied as the counter electrode and the reference electrode, respectively. The films used for characterization were prepared via the constant potential polymerization of 1.5 mM DMCS-TPA and 0.1 M TBAP in CH₂Cl₂ solutions at 1.35 V, and then measured in ACN solution containing 0.1 M TBAP as a supporting electrolyte from 0 V to 1.45

V. All the electrochemistry experiments were carried out at 25 $^\circ \rm C$ under a $\rm N_2$ atmosphere.

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