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9, 16257New thiophene-based conjugated macrocycles  
for optoelectronic applications†John Marques dos Santos, <sup>a</sup> Lethy Krishnan Jagadamma, <sup>b</sup>  
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Thiophene-based semiconductors are amongst the most successful materials in organic electronics. In this contribution, we present the synthesis and characterisation of two thiophene-based macrocycles as well as their evaluation in organic-electronic devices. **McT-1** is composed of ten thiophene moieties, whereas in **McT-2**, four additional electron-deficient benzothiadiazole moieties are incorporated to form a donor–acceptor (D–A)  $\pi$ -system. Red-shifted and broadened absorption spectra as well as more positive redox potentials are observed in **McT-2**, whereas **McT-1** displays a sharper absorption band with a higher extinction coefficient. Macrocycle **McT-1** shows emission in the yellow region whereas **McT-2** displays emission in the red wavelength region. DFT calculations predict the macrocycles to comprise of mainly the *E,E* isomers with a near-planar structure, which is further supported by the single crystal X-ray structure for **McT-1**. Their charge transporting properties are determined by fabricating thin-film OFETs. The photovoltaic properties of **McT-1** and **McT-2** are also investigated by fabricating bulk heterojunction (BHJ) devices and their potential as photodetectors has been evaluated.

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## Introduction

Small molecules and polymers used as active components of organic electronics have received a very high level of attention in recent decades owing to their wide range of attractive features including solution processability, tunable absorption and energy levels, high carrier mobility, and photochemical and thermal stability.<sup>1–9</sup> Several devices have evolved through the use of these materials, such as field-effect transistors (FETs) for microelectronics,<sup>10,11</sup> light-emitting diodes (LEDs) for lighting and displays,<sup>12–15</sup> sensors,<sup>16–18</sup> lasers,<sup>19–21</sup> molecular switches<sup>22–24</sup> and photovoltaics.<sup>25–31</sup> Despite the tremendous achievements in recent years that have led to the commercialisation of these devices, significant efforts are still devoted to enhance their performance, improve their processability and stability and understand their functionality. Hence, it is of great interest to investigate different or novel molecular systems to allow the discovery of crucial structure–activity relationships that will

allow the development of newer materials with enhanced processability and performance.<sup>32–37</sup>

In both polymer and small molecule based bulk-heterojunction (BHJ) organic photovoltaics (OPVs), the self-assembly of photoactive materials is crucial to generate efficient devices.<sup>38,39</sup> Efficient interaction between donor and acceptor materials is needed to facilitate charge separation,<sup>40</sup> and appropriate intermolecular organisation favours charge transport.<sup>41</sup> Fibre-like domains of active materials with desirable phase-separation or nanowires are often described as efficient morphologies for BHJ OPVs.<sup>36,42</sup> Molecular organisation and orientation are also important for other technologies such as organic light-emitting diodes (OLEDs)<sup>43,44</sup> and organic field-effect transistors (OFETs).<sup>45–49</sup> However, despite being an important and effective concept, the control of the construction of such assemblies is challenging.<sup>50,51</sup> In this regard, molecular recognition is promising to manipulate molecular organisation for effective self-assembly of photoactive materials.<sup>52</sup>

Conjugated macrocycles appear in this scenario as an emerging family of materials with great potential for optoelectronic applications.<sup>53–56</sup> These materials possess unique features including their controlled structure that can facilitate intermolecular arrangement,<sup>57</sup> and their defined cavity that can be used to host electronically active molecules such as fullerene derivatives.<sup>58,59</sup> Furthermore, by virtue of their cyclic structure, they do not feature end-group functionalisation, which often result in charge traps in linear molecules.<sup>53</sup> In addition, their

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Fig. 1 Scheme showing the thiophene-based macrocycles synthesised and investigated in this study.

extended conjugation with highly aligned molecular frontier orbitals often leads to desirable electronic properties such as high intramolecular charge transfer (ICT).<sup>60–62</sup> These positive features can be exploited to deliver optimum morphologies in optoelectronic devices and pave the way to more efficient charge transfer/transport.

A great number of reports have made available protocols for the synthesis of macrocycles composed of a wide variety of aromatic moieties such as: benzene, carbazole, thiophene, perylene, porphyrin, BODIPY, furan, acetylene and so forth.<sup>35,54,56,63–73</sup> Previous work reports the synthesis of cycles of different molecular lengths and cavity sizes.<sup>74,75</sup> Some also report the formation of stable supramolecular complexes with different substrates.<sup>76–81</sup> However, in spite of such interesting discoveries, examples of direct application of these interesting molecules in optoelectronic devices are still limited.<sup>58,60,82–90</sup> Some of the pioneering reports include, for instance, a triphenylamine-based compound (namely **3B2A**) reported by Zhang *et al.*,<sup>86</sup> and a perylene diimide (PDI)-based compound (namely **cPBPB**) reported by Ball *et al.* (see Fig. S1 in ESI†).<sup>55,58</sup> The former was applied as a donor material in a BHJ device showing a power conversion efficiency (PCE) of 2.66% in a blend with a fullerene derivative (**PC<sub>71</sub>BM**), whereas the latter was built to mimic fullerenes and take advantage of their useful properties such as three dimensional shape and fully delocalised  $\pi$ -space with a low lying LUMO. Interestingly, the BHJ cell incorporating **cPBPB** as the acceptor (with **PTB7-Th** as the donor) reached a PCE of 3.5% that outperformed an unfolded oligomer and a polymer of the same kind. These recent results emphasise the potential of conjugated macrocycles for optoelectronic applications.

In this contribution, we report two new thiophene-based conjugated macrocycles. Compound **McT-1** possesses a conjugated

$\pi$ -system composed of only thiophene units, whereas the formation of a donor-acceptor (D-A) system is explored in compound **McT-2** with the insertion of two benzothiadiazole (BT) moieties in each semicircular unit (Fig. 1). Thiophene moieties are found in many of the high efficiency small molecule and polymer-based OPVs<sup>27,91–96</sup> and OFET materials,<sup>10,11,46</sup> due to their excellent charge transport, high stability and polarisability, fluorescence properties and ability to form highly electron-conductive composites. Also, in comparison with benzene, thiophene shows weaker aromaticity and lower steric hindrance between neighbouring units; which leads to smaller band-gaps due to increased quinoidal character upon  $\pi$ -electron delocalisation and improved planarity.<sup>25,75,97–101</sup> Therefore, it is of great importance to investigate macrocyclic systems of this kind. Utilising the well-established McMurry reaction, alkyne-spaced building blocks were used in order to suppress steric hindrance and facilitate the cyclisation step, as is common when constructing such molecular systems.<sup>57,74</sup> However, considering results discussed in our previous report which pointed that alkyne spacers are detrimental to charge transfer, charge generation and ultimate photovoltaic performance in thiophene-based molecules,<sup>102</sup> the macrocycles were designed to minimise the number of alkyne groups compared to other reported systems, with only four present in each macrocycle. The synthesis of the new macrocycles was accomplished *via* dimerisation of two oligothiophene units, in which the concentration of the reacting species was key to yield the desired products. The UV-vis absorption and emission profiles are compared, while DFT calculations are used to investigate the nature of the electronic transitions and probe both their frontier molecular orbitals and molecular conformation. A single crystal X-ray structure was obtained for **McT-1**, from which it was possible to confirm its molecular structure and arrangement. Their potential as semiconductors is unlocked by fabricating bottom-contact OFETs and BHJ photovoltaic devices (with the macrocycles as the donor and **PC<sub>71</sub>BM** as the acceptor). Their relatively narrow spectral bandwidth allowed us to investigate their use in photodetectors without using filters in colour image sensing.

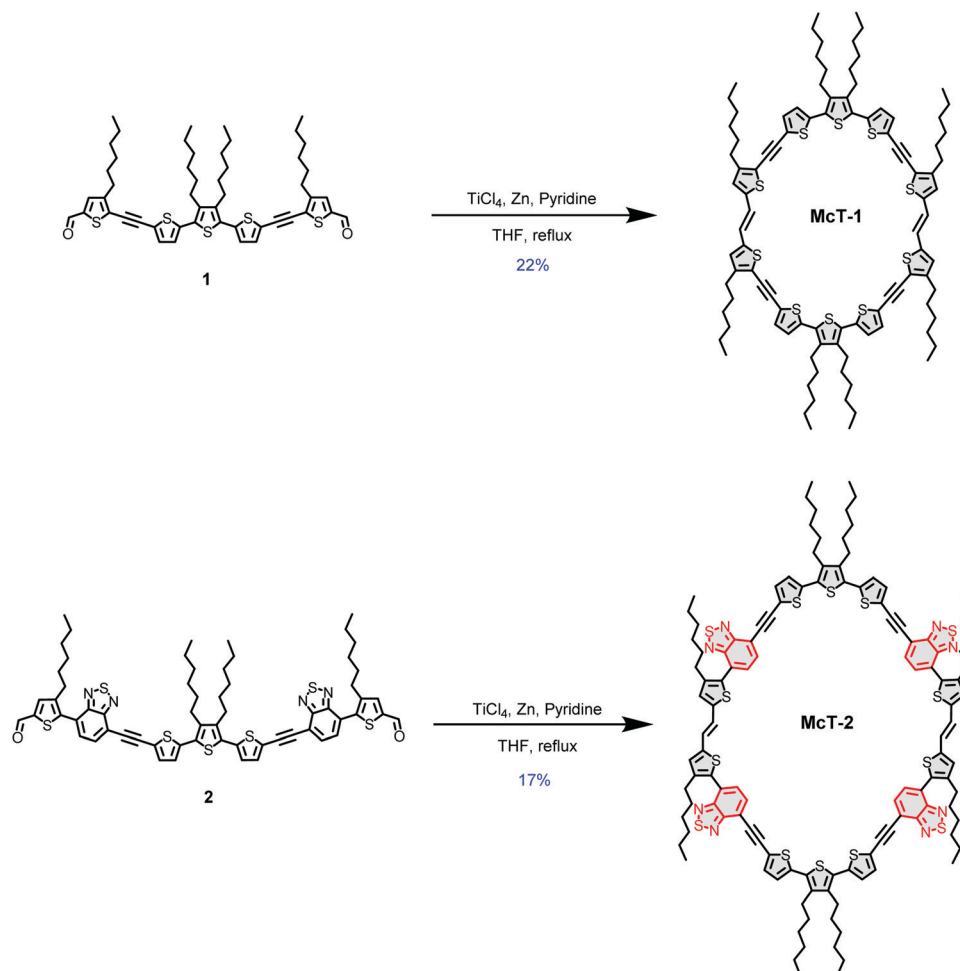
## Results and discussion

### Synthesis and molecular design

The synthetic pathway for the target molecules involved the use of Sonogashira reactions to produce the oligothiophene building blocks (see ESI†) and a McMurry coupling for the cyclisation steps (see Scheme 1). The Sonogashira cross-coupling reaction has been used extensively in the construction of these systems, providing the appropriate spacing of adjacent thiophene moieties and suppressing twisted dihedral angles.<sup>103,104</sup> However, in this work the number of alkynes were minimised, contrasting with the most common thiophene-based macrocycles reported.<sup>57,71,74</sup> This leads to a challenging molecular arrangement of the parallel thiophenes since they usually tend to arrange in an *anti*-conformation when in a linear system.<sup>92,101</sup>

In order to achieve an optimal yield by facilitating the cyclisation and suppressing polymerisation, the total concentration of





Scheme 1 Synthesis of compounds **McT-1** and **McT-2**.

the reacting species (compounds **1** and **2**) was optimised as summarised in Tables S1 and S2 (provided in the ESI<sup>†</sup>). For **McT-1**, the yield improved significantly on going from a 1.8 mM (2%) to a 3.6 mM (22%) concentration of compound **1**. For **McT-2**, only 7% yield was achieved using a 1.0 mM concentration of compound **2**, while at a 1.3 mM concentration the yield improved to 17%. In both cases, further increasing the concentration of the starting material decreased the yield considerably, possibly due to polymerisation now being more favoured.

### Thermal properties

The thermal properties of **McT-1** and **McT-2** were studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was studied to compare the thermal stability of the two macrocycles with the plots shown in Fig. S12 (ESI<sup>†</sup>). The temperature of 5% mass loss for **McT-1** was 401 °C, showing that this macrocycle has good thermal stability. However **McT-2** showed a much-reduced temperature of 5% mass loss at 228 °C and suggests that the increased strain caused by increasing the size of the macrocycle leads to a reduction in its thermal stability.

DSC plots are shown in Fig. S13 (ESI<sup>†</sup>). The heating and cooling scans for **McT-1** show no obvious phase transitions between 25 °C and 300 °C, which is an advantage for device

processing as the material can be annealed without crystallisation and subsequent formation of grain boundaries. On heating **McT-2**, there is a melt peak at 50.1 °C and in the reverse scan the peak at 45.5 °C indicates crystallisation upon cooling. This phase change at relatively low temperature may be detrimental to device performance.

### Optical and electrochemical properties

The absorption spectra of both macrocycles ( $5 \times 10^{-6}$  M in  $\text{CH}_2\text{Cl}_2$ ) are shown in Fig. 2. **McT-1** showed a weak absorbance band in a shorter wavelength region, *ca.* 300 nm, and a sharp, strong absorbance band at 438 nm (maximum absorbance,  $\lambda_{\text{max}}$ ) (Fig. 2(a)). **McT-2**, however, presented two strong absorbance peaks at shorter wavelengths (*ca.* 325 nm and 375 nm) and a  $\lambda_{\text{max}}$  at 476 nm (Fig. 2(b)). The bands at maximum absorbance are often a result of  $S_0-S_1$  and  $S_0-S_2$  type transitions.<sup>72</sup> Notably, this band red-shifts for the BT-containing macrocycle **McT-2** (*ca.* 30 nm) with respect to **McT-1**, with the former also showing a broader spectrum and a high absorbance throughout most of the region covered. This phenomenon is ascribed to a pronounced ICT effect since the electron-withdrawing BT moieties induce a push-pull effect in this D-A system. Furthermore, new bands observed at around 320–400 nm are likely originating from the BT unit's



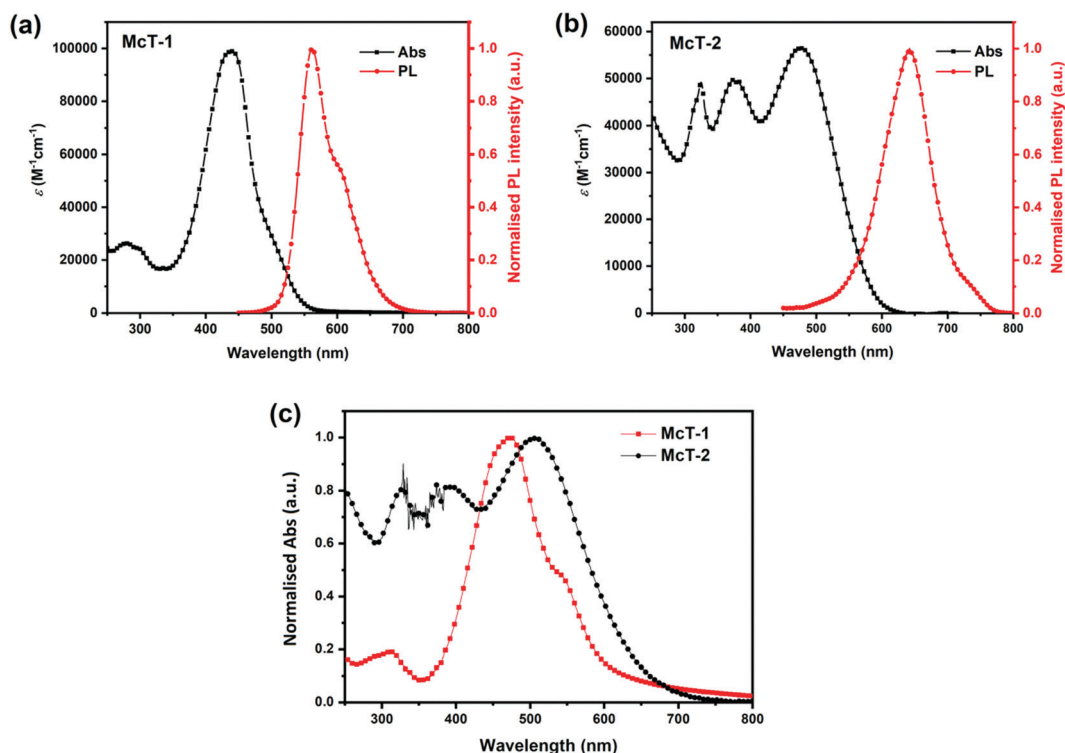


Fig. 2 Absorption and fluorescence spectra of **McT-1** (a) and **McT-2** (b) in solution state ( $\text{CH}_2\text{Cl}_2$ ,  $5 \times 10^{-6}$  M) (the fluorescence spectra were excited at 440 and 480 nm for **McT-1** and **McT-2**, respectively). (c) Normalised absorption spectra of **McT-1** and **McT-2** in thin film form.

$\pi$ - $\pi^*$  internal transition.<sup>105</sup> On the other hand, the simplest macrocyclic compound (**McT-1**) presented a higher value of extinction coefficient ( $\epsilon_{\text{max}}$ ,  $98\,890\text{ M}^{-1}\text{ cm}^{-1}$ ) than its BT-containing analogue ( $56\,560\text{ M}^{-1}\text{ cm}^{-1}$ ). Values relating to the onset of absorbance ( $\lambda_{\text{onset}}$ ) were estimated as 561 nm for **McT-1** and 612 nm for **McT-2**, and correspond to optical band-gap ( $E_{\text{opt}}$ ) values of 2.21 eV and 2.02 eV, respectively. In thin films (Fig. 2(c)), the two macrocycles present bathochromic shifts in  $\lambda_{\text{max}}$  (ca. 30 nm), typically as a result of enhanced  $\pi$ - $\pi$  stacking interactions. Furthermore, the main absorbance band is broadened and extends to longer wavelength for both compounds, while for **McT-1** the insurgence of a shoulder at ca. 545 nm is seen which is perhaps a vibronic level or due to  $\pi$ - $\pi$  stacking. The optical data are summarised in Table 1.

The emission spectra of the two macrocycles were recorded in solution (Fig. 2(a and b)). **McT-1** shows an emission peak at 560 nm (with a vibronic shoulder around 600 nm) and **McT-2** presents a peak at 642 nm with reasonably sharp full-width at

half-maximum (FWHM) (ca. 70 nm for **McT-1** and 82 nm for **McT-2**). It is also noteworthy that both compounds have large Stokes shifts despite the circularly locked structure. The Stokes shift was higher for **McT-2** (ca. 166 nm) than for **McT-1** (122 nm), possibly due to rotation of the BT units after excitation.<sup>106-108</sup> A larger Stokes shift has also been observed in a BT-containing [10]cycloparaphenylene (**BT[10]CPP**) compared to its parent [10]CPP.<sup>109</sup>

To study the possible interactions between the macrocycles and fullerenes, fluorescence titration was performed with **McT-1** and **McT-2** in toluene solution, since fluorescence quenching can be indicative of intermolecular interactions.<sup>110,111</sup> This was done through the addition of aliquots of a solution of  $\text{C}_{60}$  in toluene. When analysing the fluorescence intensity upon addition of small amounts of  $\text{C}_{60}$  (see Fig. S14, ESI<sup>†</sup>), one can notice a substantial quenching happening only after a considerable increase of  $\text{C}_{60}$  concentration in both cases. In fact, ca. 65% of the intensity was only quenched after an addition of ca. 300 equivalents of  $\text{C}_{60}$  to 1 equivalent of **McT-1** and ca. 125 equivalents of  $\text{C}_{60}$  to 1 equivalent of **McT-2**. According to these

Table 1 Summary of optical and electrochemical data of **McT-1** and **McT-2**

Dye	$\lambda_{\text{max/abs}}^a$ (nm)	$\epsilon_{\text{max}}^a$ ( $\text{M}^{-1}\text{ cm}^{-1}$ )	$\lambda_{\text{max}}^b$ (nm)	$\lambda_{\text{max/emi}}^a$ (nm)	$\lambda_{\text{onset}}^a$ (nm)	$E_{\text{opt}}^c$ (eV)	$E_{1/2\text{ox}}^d$ (V)	$E_{1/2\text{red}}^d$ (V)	IE <sup>e</sup> (eV)	EA <sup>f</sup> (eV)	$E_{\text{fund}}^g$ (eV)
<b>McT-1</b>	438	98 890	473	560	561	2.21	0.17	-1.88	-5.0	-2.9	2.1
<b>McT-2</b>	476	56 560	502	642	612	2.02	0.03	-1.62	-4.8	-3.2	1.6

<sup>a</sup> Measured in dichloromethane ( $5 \times 10^{-6}$  M). <sup>b</sup> Measured in thin film. <sup>c</sup> Calculated using the formula  $E_{\text{opt}} = 1240/\lambda_{\text{onset}}$ . <sup>d</sup> Measured by square wave voltammetry in dichloromethane ( $1 \times 10^{-3}$  M) and calibrated versus the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple. <sup>e</sup> Calculated using the formula  $\text{IE} = -[E_{\text{ox}} + 4.8]$  eV.<sup>114</sup> <sup>f</sup> Calculated using the formula  $\text{EA} = -[E_{\text{red}} + 4.8]$  eV.<sup>114</sup> <sup>g</sup> Calculated using the formula  $E_{\text{fund}} = |\text{IE} - \text{EA}|$  eV.<sup>114</sup>





Fig. 3 Cyclic voltammograms of **McT-1** (a) and **McT-2** (b). The voltammograms were recorded in  $\text{CH}_2\text{Cl}_2$  solution ( $1 \times 10^{-3}$  M). The electrodes used were a 1.6 mm diameter platinum working electrode, a platinum wire counter electrode and a silver wire quasi-reference electrode and the electrolyte of choice was TBA-PF<sub>6</sub> (0.1 M). Voltammograms were calibrated versus the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple as an external standard. In (c) the energy level diagram of **McT-1**, **McT-2** and the **PC<sub>71</sub>BM** acceptor (obtained from the literature) is provided.<sup>112,113</sup>

results, we hypothesised that limited cavity filling or complexation between the McT series and C<sub>60</sub> took place in these solutions.

Cyclic voltammetry (CV) and square wave voltammetry (SWV) were used to study the electronic properties of the two molecules. The CV measurements revealed one clear oxidation wave with non-reversible character for **McT-1**, whereas for **McT-2**, three low intensity irreversible peaks at ca. 0.0 V, 0.4 V and 0.6 V and a quasi-reversible reduction wave was seen [Fig. 3(a and b)]. The SWV measurements revealed in turn a clearer peak of reduction for **McT-1** and two clear reduction peaks for **McT-2** (Fig. S15, ESI<sup>†</sup>). Utilising the SWV values to estimate the energy levels, the ascribed first reduction peak ( $E_{1/2\text{red}}$ ) of **McT-2** is more positive than for its counterpart, resulting in a lower-lying electron affinity (EA, -3.2 eV) than for **McT-1** (-2.9 eV). The first oxidation peak ( $E_{1/2\text{ox}}$ ) of **McT-1** was found at 0.17 V, resulting in a high-lying ionisation energy (IE) of -5.0 eV. These low values of  $E_{1/2\text{ox}}$  and shallow IE are typical of these types of thiophene-based macrocycles.<sup>57,72,76</sup> Surprisingly, a higher IE was observed for electrochemical measurements performed on **McT-2** (-4.8 eV). Hence, based on these data, both **McT-1** and **McT-2** are considered donor type materials, with a fundamental gap ( $E_{\text{fund}}$ ) of 2.1 eV and 1.6 eV, respectively (in accordance with the  $E_{\text{opt}}$  obtained from

solution), and can be used with **PCBMs** as acceptors in BHJ cells (see energy level diagram in Fig. 3(c)).<sup>112,113</sup> The electrochemical data are given in Table 1.

### Theoretical calculations

Compounds **McT-1** and **McT-2** were studied using density functional theory (DFT) calculations (B3LYP/6-311G(d,p) level of theory in the gas-phase) to investigate their dihedral angles, conformation and frontier orbital distribution. To gain insight into whether these specific macrocycles would be generated as *E,E* or *Z,Z* isomers, **McT-2** was first calculated in both forms (*E,E* and *Z,Z*) and the total energies of both analogues were compared upon geometry optimisation (see Fig. S16 in ESI<sup>†</sup>). A considerably strained conformation was observed for the *Z,Z* isomer of **McT-2**, whereas the *E,E* isomer is more planar (Fig. S16, ESI<sup>†</sup>). For the *E,E* isomer, the central thiophene moiety (T1) is allocated *syn* to its two peripheral neighbours (T1 and T10), whereas for the *Z,Z* isomer it is allocated *anti* [see Fig. 4(a) for atom and moiety labels]. A considerably higher bond angle of the vinyl group (bond angle C24-C25-C26 137°) was observed for the *Z,Z* isomer of **McT-2** than for *E,E* isomer of **McT-2** (126°), which implies that the *Z,Z* isomer has a more



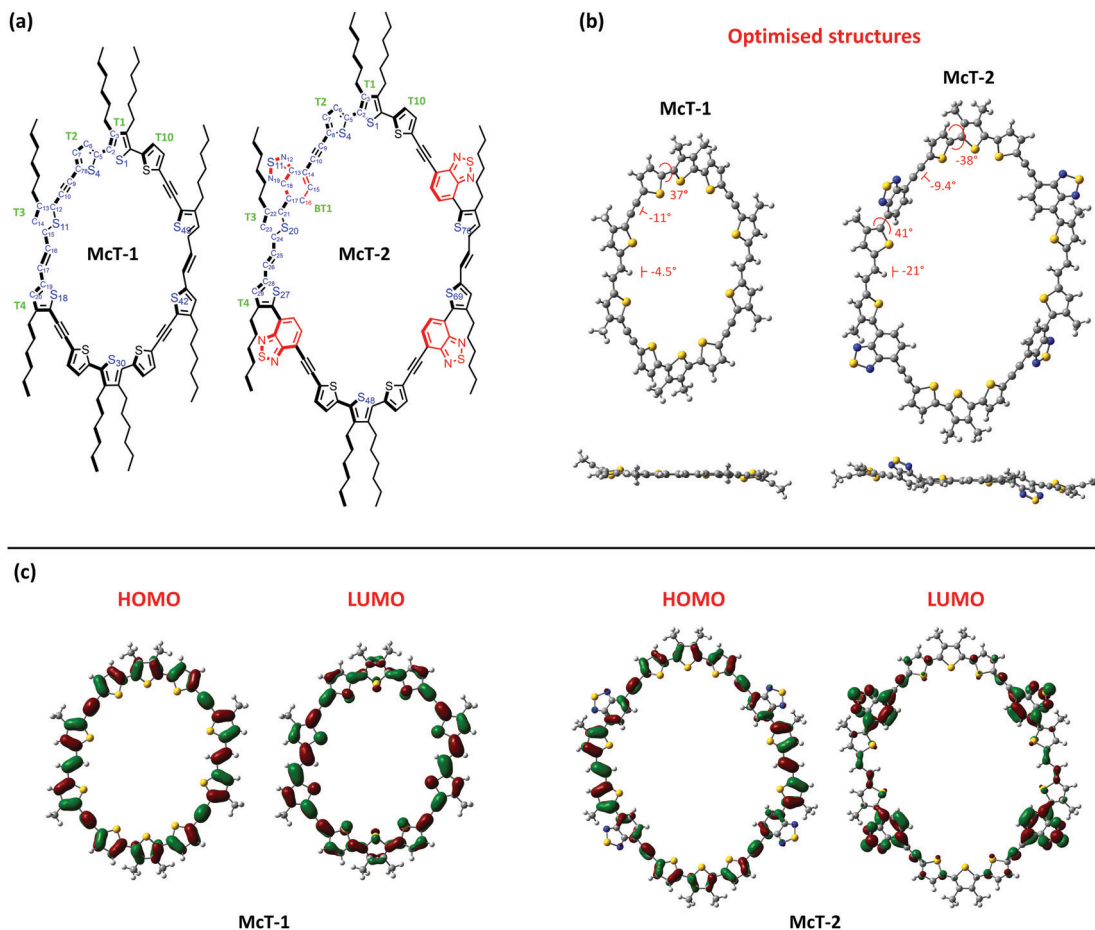


Fig. 4 (a) Illustration of molecular structure of **McT-1** and **McT-2** showing atom labels (T1–10 represents thiophene moieties). (b) Optimised structures from DFT (B3LYP/6-311G(d,p)) of **McT-1** and **McT-2** (diagonal and side views). (c) HOMO and LUMO maps of **McT-1** and **McT-2**.

strained circular structure. A difference of  $22 \text{ kJ mol}^{-1}$  was found between the *E,E* and the *Z,Z* isomers ground state total energy, with the *E,E*-isomer being the lowest in energy. In the literature, similar compounds with a more regular ratio of alkyne spacers are shown to cyclise in both forms.<sup>76,77</sup> However, due to such strain observed for the *Z,Z* isomer, it was expected that both macrocycles are present as mainly their *E,E* isomers since the transition state conformation in the final synthetic step is likely to affect the activation energy to form the product. In such forms, both compounds show near-planar structure. For **McT-1** only the central thiophene moiety (T1) shows a moderate dihedral angle with its neighbouring moieties (T2 and T10) (*i.e.* torsion angle S1–C2–C5–S4  $36.5^\circ$ ) [Fig. 4(b)], whereas **McT-2** presents a notable dihedral angle of  $41.1^\circ$  also between the moieties T3 and BT1 (C16–C17–C21–S20) due to the alkyl chain.

The ring size is naturally wider/bigger for **McT-2** since it contains 4 more aromatic moieties than **McT-1**. According to the calculations, the cavity size varies between 12.9 Å (S11...S42) to 16.2 Å (S1...S30) for **McT-1** and between 20.1 Å (S20...S69) to 22.8 Å (S1...S48) for **McT-2**. Therefore, it is reasonable to assume that both compounds possess sufficiently large cavities to accommodate guest molecules such as fullerenes.  $\text{C}_{60}$  for instance, has a mean ball diameter of 7.1 Å, whereas  $\text{C}_{70}$  has a

short axis of 7.1 Å and a long axis of 7.9 Å.<sup>115</sup> However, due to the absence of alkyne spacers between several thiophene moieties in the macrocycles, both adopt elliptical-like structures. This could potentially discourage fullerene molecules filling the cavity due to steric reasons. This will be especially true for **McT-1**, as the cavity has a considerably shorter axis than the other macrocycle. The frontier orbitals, depicted in Fig. 4(c), are completely delocalised in the case of **McT-1** with a total overlap of HOMO and LUMO. The distribution is different for **McT-2**, where the HOMO appears delocalised along the whole molecule but the LUMO is mostly confined over the BT moieties. This is mainly due to the push-pull system generated with the introduction of the BT moieties, which also causes the red-shift in the UV-vis spectrum. The calculated HOMO ( $-4.83 \text{ eV}$  for **McT-1** and  $-5.09 \text{ eV}$  for **McT-2**) and the LUMO ( $-2.57 \text{ eV}$  for **McT-1** and  $-3.01 \text{ eV}$  for **McT-2**) energy levels (Fig. S17, ESI<sup>†</sup>) are in good agreement with the IE and EA values obtained experimentally for **McT-1**, whereas for **McT-2** the HOMO is lower than the experimentally derived value (see Table S3, ESI<sup>†</sup>).

Time-dependent DFT calculations were performed to gain more insight into the optical properties of the materials. These were conducted using the same method (B3LYP/6-311G(d,p) in the gas-phase). The calculations provided a reasonable



estimation of the absorption spectrum similar to the experimental data presented in Fig. 2 and Table 1 for both **McT-1** and **McT-2** (Fig. S18, ESI<sup>†</sup>). Upon analysing the electronic transitions responsible for the main bands of absorption observed for the two molecules (Tables S4 and S5, ESI<sup>†</sup>), we observed that in both cases the highest wavelength absorbance bands (around 500 nm for **McT-1** and 630 nm for **McT-2**) are composed of four excited states ( $S_2, S_3, S_4$  and  $S_6$  for **McT-1**, and  $S_2, S_3, S_4$  and  $S_7$  for **McT-2**). This band is dominated by a transition from the HOMO–1 to the LUMO ( $S_0 \rightarrow S_3$ ) for **McT-1** and from the HOMO to the LUMO+1 ( $S_0 \rightarrow S_2$ ) for **McT-2**, the latter being ICT in nature. The lower wavelength absorbance (*ca.* 370 nm for **McT-1** and *ca.* 440 for **McT-2**) splits between two main excited states ( $S_{16}$  and  $S_{17}$  for **McT-1**, and  $S_{21}$  and  $S_{23}$  for **McT-2**), resulting from a strong contribution of HOMO–1 to LUMO+4 for **McT-1** and HOMO to LUMO+6 for **McT-2**. Plots of selected molecular orbital density maps is provided in Fig. S19 (ESI<sup>†</sup>) for **McT-1** and Fig. S20 (ESI<sup>†</sup>) for **McT-2**, including those involved in the strongest transitions described here. These orbitals are also delocalised mostly along the whole molecule for **McT-1**, whereas for **McT-2** the LUMO+6 is also delocalised over the thiophenes T3, T4, T8 and T9 and the vinyl residues.

### X-Ray structures

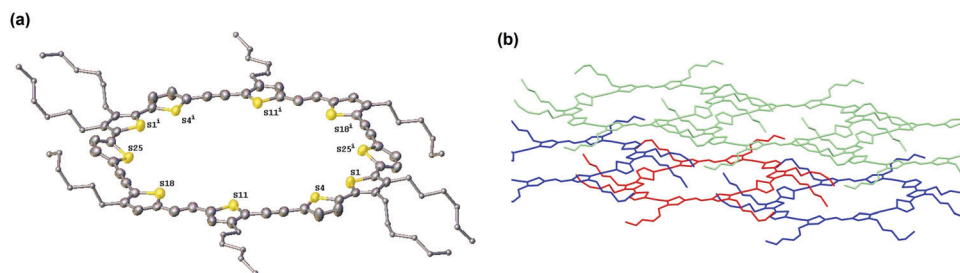
Single crystals of **McT-1** were obtained from slow diffusion of heptane in a benzene solution, and its structure was determined by X-ray analysis. Unfortunately, attempts to obtain single crystals of **McT-2** were unsuccessful. The X-ray crystal structure of **McT-1** (Fig. 5(a)) shows all the thiophene sulfur atoms face into the centre of the macrocycle and is consistent with the calculated prediction that the vinyl groups would be *E*-isomers. **McT-1** crystallises with half the molecule in the asymmetric unit and the other half is related by inversion symmetry. The two crystallographically independent alkyne bonds have different conformations, with one having two almost exactly coplanar thiophene rings (angle between mean planes  $0.99^\circ$ ) and the other with the two rings tilted at  $27.75^\circ$  to one another. The three linked thiophene rings have two rings essentially coplanar (torsion angles  $S4-C5-C2-S1 -2.0(8)^\circ$ ) and the other two tilted at  $\sim 30^\circ$  (torsion angle  $S25-C29-C30-S1i -31.3(8)^\circ$ ). Apart from this tilted thiophene ring the macrocycle is essentially planar. The alkyl chain substituents on the central S1 thiophene both lie out of the

plane on the same side for a given thiophene ring (also the same side for adjacent ring S18) and on the opposite side to the symmetry equivalent S1 thiophene on the other side of the macrocycle. The  $S1 \dots S1(i)$  distance is  $16.406(2)$  Å and  $S18 \dots S11(i)$   $12.423(2)$  Å. Examination of the packing in **McT-1** (Fig. 5(b) and Fig. S21, ESI<sup>†</sup>) shows that the cavities are filled by the alkyl chains from adjacent molecules. Each cavity contains four chains in total with two each from adjacent S1 two pointing downwards and two upwards forming zig-zag chains. These chains are then ‘cross-linked’ by the  $S \dots S$  contacts between the two S atoms across the other pair of alkyne bonds (S4 and S11) with an adjacent chain at approximately the sum of the van der Waals radii at just under  $3.6$  Å. The adjacent chain is shown in green in Fig. 5(b).

### Organic field-effect transistors

The charge transporting properties of the macrocycles were studied in bottom-gate, bottom-contact OFETs. **McT-1** was deposited in two different solutions, chloroform and toluene, to determine whether this influenced the performance of the OFETs. Devices containing **McT-2** did not show any field-effect in either p-type or n-type transistors. This may be explained by the increased twisting in the macrocycle as a result of introducing the benzo-thiadiazole unit, as shown by theoretical calculations in Fig. 4b. DSC data also showed that there is a relatively low melt temperature which suggests **McT-2** may undergo a phase change when a voltage is applied across the channel, particularly if there is a high resistance. Moreover, **McT-2**, showed weak oxidation peaks in cyclic and square-wave voltammetry experiments, suggesting that it may be a poor p-type material.

Examples of the OFET characteristics for **McT-1** containing OFETs are shown in Fig. 6 and a summary of the averaged data is presented in Table 2. There are small differences in performance of the OFETs when the solvent is varied. The p-type mobilities are similar at  $1.92 \pm 0.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  when deposited from toluene and  $1.66 \pm 0.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  when chloroform is used. The on/off ratios are relatively low at  $10^2$  which is mainly caused by the relatively low ON current, due to the limited hole mobility, but also partly due to a higher OFF current due to relatively short channel lengths (5, 10 and 20  $\mu\text{m}$ ). The main difference is in the threshold voltage which is slightly reduced for OFETs fabricated using toluene. These differences may be influenced by the slower drying of toluene compared to chloroform.



**Fig. 5** (a) View showing **McT-1** in the crystal structure (H atoms and minor alkyl chain disorder components omitted for clarity, displacement ellipsoids drawn at 50% probability level while alkyl chains drawn as spheres of arbitrary radius). The two halves of the molecule are related by an inversion centre ( $i = 1 - x, -y, -z$ ). (b) Shows that the cavities are filled by the four alkyl chains, 2 each from adjacent molecules (shown in blue); an adjacent chain is shown in green.



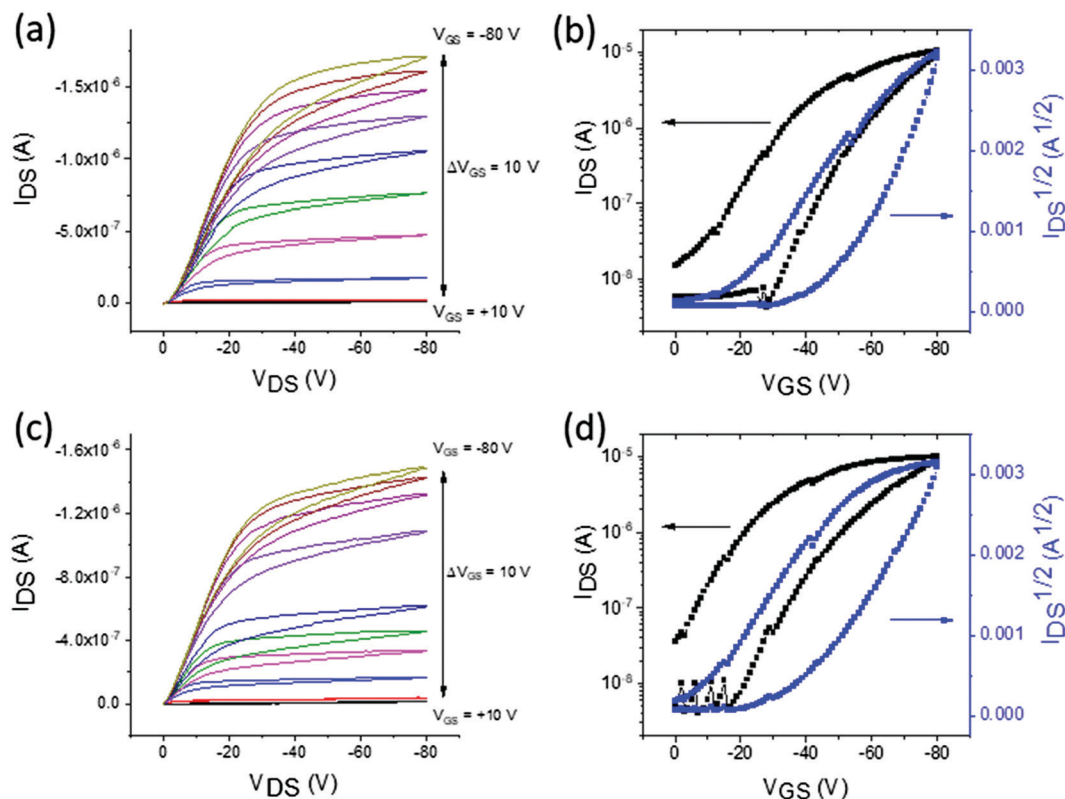


Fig. 6 Characterisation of OFETs fabricated using **McT-1**, channel length = 10  $\mu\text{m}$ , channel width = 1cm. Output characteristics of OFETs fabricated using **McT-1** in (a) chloroform and (c) toluene solutions. Transfer graphs for **McT-1** films deposited using (b) chloroform and (d) toluene solutions where  $V_{\text{DS}} = -70$  V.

Table 2 Summary of OFET performance of **McT-1** deposited from chloroform and toluene solutions

Solvent	On/off ratio	$V_{\text{th}}$ [V]	$\mu_{\text{h}}$ [ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ]
Chloroform	$10^2$	-9	$1.66 \pm 0.6 \times 10^{-4}$
Toluene	$10^2$	-1	$1.92 \pm 0.8 \times 10^{-4}$

Atomic force microscopy was used to study the difference in the topographies of the films. Images with scan area  $10 \times 10 \mu\text{m}^2$  are presented in Fig. 7 as well at  $5 \times 5 \mu\text{m}^2$  and  $20 \times 20 \mu\text{m}^2$  in

Fig. S22 and S23 (ESI<sup>†</sup>), respectively. The general topographies show similarities, with holes emerging in both films. However, the film deposited from chloroform shows smaller, more isolated domains whilst the films formed from toluene show larger domains although there are still pinholes present. The difference in topographies may result from the lower boiling point of chloroform causing quicker drying of the film. The gaps observed in the morphology of both films could help to explain the low mobilities measured, since charge transport will be limited with so many disconnections in the bulk. However, the closeness of

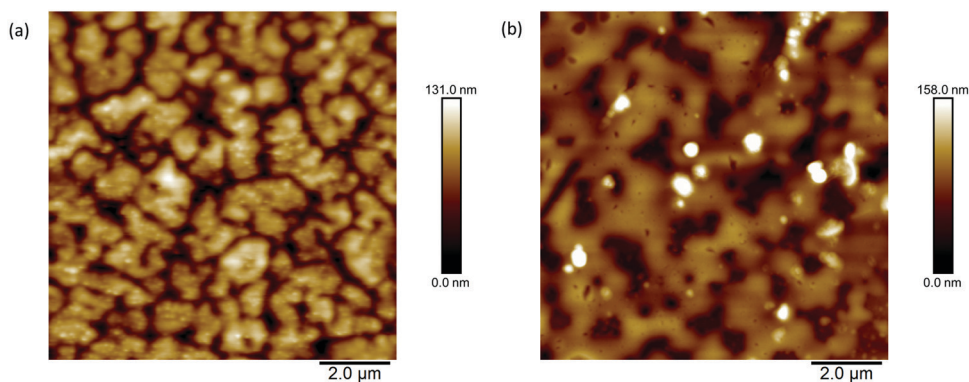


Fig. 7 Tapping mode atomic force microscopy images of **McT-1** films deposited from (a) chloroform (RMS roughness = 17.8 nm) and (b) toluene (RMS roughness = 22.8 nm) solutions on prefabricated OFET substrates. Scan area =  $10 \times 10 \mu\text{m}^2$ .





the general topographies is consistent with the similar calculated hole mobilities.

### Photovoltaic properties

To investigate the photovoltaic properties of **McT-1** and **McT-2**, bulk heterojunction solar cells were fabricated using **PC<sub>71</sub>BM** as the acceptor. Before proceeding with device fabrication, charge transfer of **McT-1** and **McT-2** donors to the **PC<sub>71</sub>BM** acceptor was investigated using photoluminescence quenching studies. Efficient charge transfer from the donor to acceptor will quench the photoluminescence of the donor molecules. The steady-state luminescence spectra of the neat donor molecules and their blends with **PC<sub>71</sub>BM** for different weight ratios (1:1, 1:2, 1:3 and 1:4) are shown in Fig. 8(a and b). With the addition of **PC<sub>71</sub>BM**, for both donor molecules, the photoluminescence is significantly quenched which implies that there is efficient charge transfer from the donors **McT-1** and **McT-2** to the acceptor. The UV-Vis absorption properties of these different blend films are shown in Fig. 8(c and d). For both the blends the absorption bandwidth is narrow and mainly in the region 400–600 nm.

With the efficient charge transfer properties confirmed through the PL quenching, solution-processed organic solar

cells were fabricated for both **McT-1** and **McT-2** using different donor:acceptor (**PC<sub>71</sub>BM**) ratios of 1:1, 1:2, 1:3 and 1:4. The photovoltaic performance parameters of the corresponding blend films are shown in Table 3 and the *J-V* characteristics are shown in Fig. 9(a and b). For **McT-1** with the increase of **PC<sub>71</sub>BM** content, the power conversion efficiency increases and at the optimised blend ratio of 1:4, the corresponding solar cells show an efficiency of ~1.1%. Photovoltaic devices with higher blend ratios were not fabricated since the power conversion efficiencies for the 1:3 and 1:4 blends are very similar. For **McT-2:PC<sub>71</sub>BM** blends, a similar trend is seen and the highest efficiency of 0.63% is obtained for 1:3 donor:acceptor ratio.

For both **McT-1** and **McT-2**, with the increase in **PC<sub>71</sub>BM** content, the short circuit current density ( $J_{sc}$ ) increased and a corresponding increase in power conversion efficiency is obtained (shown in Table 3). This increase in photovoltaic properties with increase in fullerene content has been previously reported for oligothiophene: fullerene BHJ blends.<sup>99,116,117</sup> With increase in fullerene content, crystallisation of the macrocycles is prevented by the fullerenes, resulting in a BHJ morphology with enhanced mixing, favouring the exciton dissociation and photocurrent. Moreover, increased fullerene content has also been

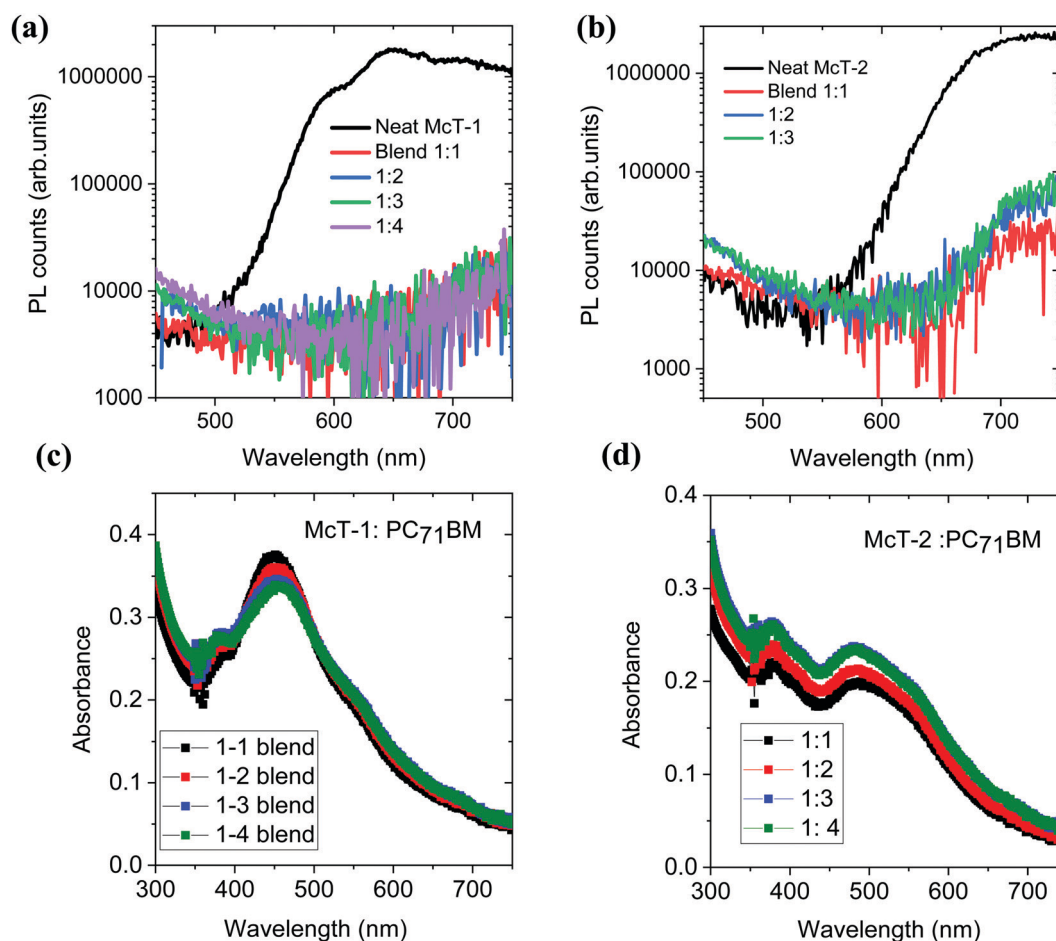


Fig. 8 Steady state photoluminescence spectra of (a) neat **McT-1** and blend with **PC<sub>71</sub>BM** for different ratios (b) neat **McT-2** and blend with **PC<sub>71</sub>BM** for different ratios. The excitation wavelength is 450 nm. Absorbance spectra of the (c) **McT-1** and **PC<sub>71</sub>BM** blends (d) **McT-2** and **PC<sub>71</sub>BM** blends as a function of different blend ratios.



Table 3 Photovoltaic performance parameters of the **McT-1:PC<sub>71</sub>BM** and **McT-2:PC<sub>71</sub>BM** blends for different D:A weight ratios

Blend	D:A (wt.) ratio	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	FF (%)	$R_{sh}$ ( $\Omega$ cm <sup>2</sup> )	$R_s$ ( $\Omega$ cm <sup>2</sup> )	PCE avg (%)	PCE best (%)
<b>McT-1 and PC<sub>71</sub>BM</b>	1-1	2.84 ± 0.70	0.699 ± 0.011	33.6 ± 1.0	453 ± 31	10.3 ± 1.2	0.67 ± 0.05	0.73
	1-2	3.74 ± 0.18	0.683 ± 0.033	33.7 ± 1.7	357 ± 64	5.3 ± 1.6	0.86 ± 0.10	0.97
	1-3	3.86 ± 0.35	0.669 ± 0.019	35.3 ± 1.2	341 ± 33	3.0 ± 1.3	0.91 ± 0.11	1.05
	1-4	4.08 ± 0.29	0.662 ± 0.018	35.0 ± 0.9	303 ± 29	3.4 ± 1.3	0.95 ± 0.09	1.07
<b>McT-2 and PC<sub>71</sub>BM</b>	1-1	1.62 ± 0.13	0.401 ± 0.047	29.9 ± 0.3	361 ± 46	5.4 ± 1.4	0.20 ± 0.03	0.23
	1-2	2.25 ± 0.21	0.421 ± 0.038	31.4 ± 0.4	300 ± 40	2.7 ± 1.2	0.30 ± 0.04	0.34
	1-3	2.59 ± 0.26	0.682 ± 0.057	28.9 ± 1.1	392 ± 30	3.6 ± 1.5	0.51 ± 0.07	0.63
	1-4	2.62 ± 0.19	0.604 ± 0.077	29.5 ± 1.1	348 ± 39	3.1 ± 1.3	0.47 ± 0.08	0.58

reported in better percolative carrier transport pathways. However, for both donors, the main limiting factors of the photovoltaic properties are the low short circuit current density (1.6–4.0 mA cm<sup>-2</sup>) and the fill factor which is below 40% even for the optimised donor:acceptor blend. One of the main contributing factors for the low  $J_{sc}$  is the narrow absorption bandwidth in the visible region. The low FF implies unfavourable nanoscale morphology of the donor:acceptor blends preventing efficient collection of photogenerated charges. For both **McT-1** and **McT-2**, under the optimised donor: acceptor blend condition, the open circuit voltage is very similar  $\sim$ 0.67 V. Considering the HOMO level of the **McT-1** and LUMO level of the **PC<sub>71</sub>BM** as shown in Fig. 3(c), a voltage loss of less than 0.2 V is seen for the optimised

blend of **McT-1:PC<sub>71</sub>BM**. **McT-2** showed in general slightly poorer  $V_{oc}$  than **McT-1** due to its higher HOMO level.

The external quantum efficiency (EQE) spectra of the **McT-1:PC<sub>71</sub>BM** and **McT-2:PC<sub>71</sub>BM** blends are shown in Fig. 9(c and d). For both donors, EQE increases with increase in **PC<sub>71</sub>BM** content and this agrees with the increase in  $J_{sc}$  shown in Table 3. Under the optimised blend ratio of 1:4, **McT-1:PC<sub>71</sub>BM** shows an EQE of  $\sim$ 40% and for **McT-1:PC<sub>71</sub>BM**, the EQE is slightly lower around 25% in the 350 to 550 nm range. Because of the narrow spectral bandwidth of the UV-Vis absorption profile and the EQE spectra of the **McT-1:PC<sub>71</sub>BM** and **McT-2:PC<sub>71</sub>BM**, the spectral responsivity is estimated as a function of wavelength towards their use in photodetectors. The narrow spectral

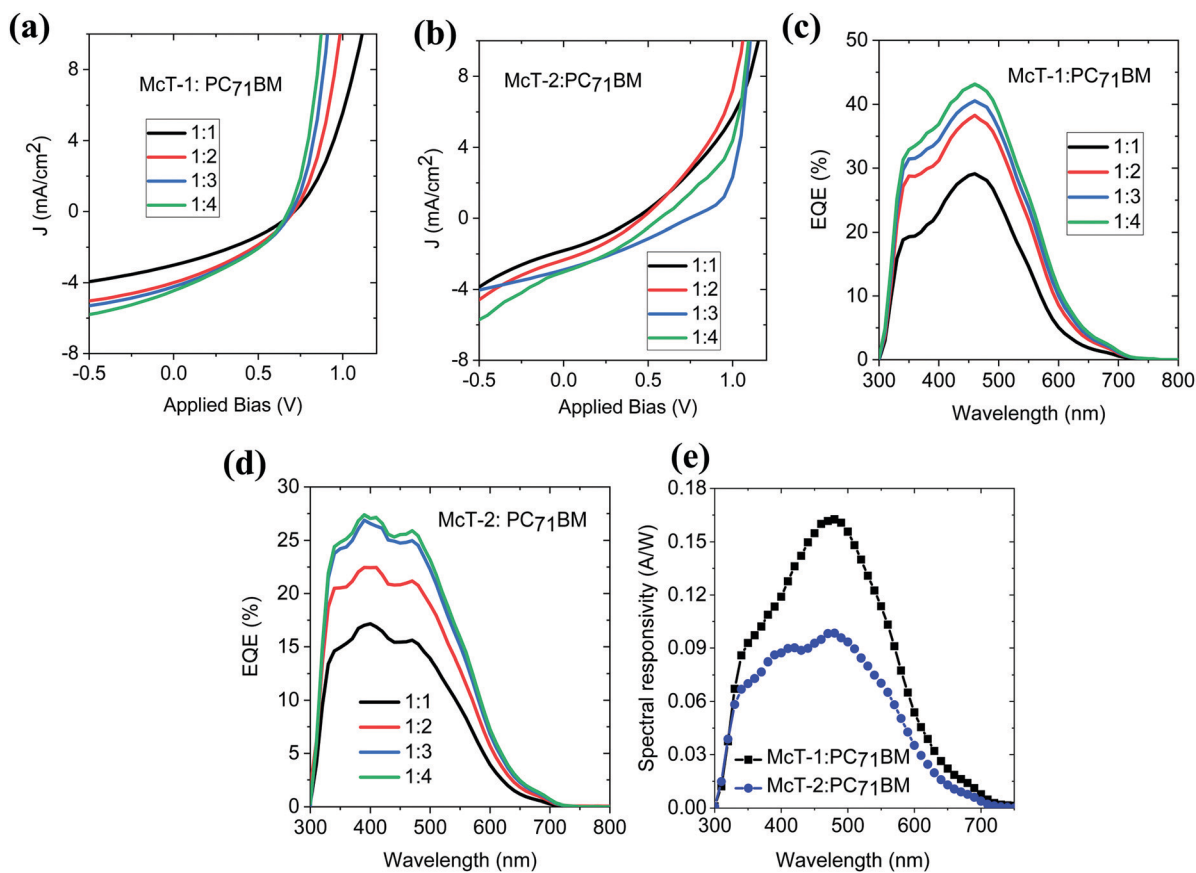


Fig. 9  $J$ - $V$  characteristics of the (a) **McT-1:PC<sub>71</sub>BM** and (b) **McT-2:PC<sub>71</sub>BM** blends as a function of different blend ratios. External quantum efficiency (EQE) spectra of the (c) **McT-1:PC<sub>71</sub>BM** and (d) **McT-2:PC<sub>71</sub>BM** blends as a function of different blend ratios. (e) Spectral responsivity curves of the corresponding photovoltaic devices estimated from their EQE spectra.



bandwidth allows them to be used in photodetector applications without the use of filters in colour image sensing.<sup>1,118</sup> The corresponding spectral responsivity curves for the optimised blend ratios are shown in Fig. 9(e). For the **McT-1:PC<sub>71</sub>BM** blend, a maximum responsivity of 0.16 A W<sup>-1</sup> at 478 nm, and for **McT-2:PC<sub>71</sub>BM**, 0.10 A W<sup>-1</sup> at 478 nm are obtained under zero external bias. This zero bias responsivity values obtained are comparable to the previously reported responsivity of organic photodiodes such as **P3HT:ICBA**, **P3HT:PC<sub>60</sub>BM** blends<sup>119,120</sup> and better than the recently reported responsivity of pentacene:C<sub>60</sub> heterostructure<sup>121</sup> in the blue wavelength range. This blue wavelength responsivity of **McT-1:PC<sub>71</sub>BM** blend is relevant for the development of organic photodetectors without colour filters for imaging applications.

## Conclusions

In conclusion, we show that incorporating an electron-deficient benzothiadiazole unit within a thiophene-based macrocycle red-shifts and broadens the main band of absorption while improving the absorbance in higher energy wavelengths, whereas the simplest macrocycle **McT-1** shows a higher  $\epsilon_{\text{max}}$  value. DFT calculations indicated that the macrocycles would possess a high level of planarity with *E,E*-isomers being preferred, and in the case of **McT-1** this prediction was further indicated by crystallographic data. The theoretical calculations also revealed the ICT character of **McT-2**, which has a striking impact on the absorption profile. Organic field-effect transistors were fabricated, with **McT-1** exhibiting a hole mobility of  $1.92 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Efficient charge transfer between the macrocycles and **PC<sub>71</sub>BM** acceptor was revealed by photoluminescence quenching studies and led us to investigate them in photovoltaic devices. For both macrocycles, the photovoltaic cells showed an increase in  $J_{\text{sc}}$  with concomitant increase of power conversion efficiency with the increase in **PC<sub>71</sub>BM** content. The cells displayed an optimal efficiency of ~1.1% for the 1:4 **McT-1:PC<sub>71</sub>BM** blend and 0.63% 1:3 for the **McT-2:PC<sub>71</sub>BM** blend. The improvement in spectral absorption did not produce higher  $J_{\text{sc}}$  in the case of **McT-2** presumably due to unfavourable nanoscale morphology preventing efficient charge collection, as indicated by the OPV data. This is also likely due to the presence of alkyne residues, which tend to affect charge generation and OPV performance. For future studies of related macrocycles in OPVs, we encourage the total removal of alkyne residues and further investigation of the self-assembly of these molecules. In photodetectors, the **McT-1:PC<sub>71</sub>BM** and **McT-2:PC<sub>71</sub>BM** blends showed a maximum responsivity of 0.16 A W<sup>-1</sup> at 478 nm, and 0.10 A W<sup>-1</sup> at 478 nm, respectively, under zero external bias. This is a relevant result for the field of organic photodetectors without colour filters for imaging applications.

## Conflicts of interest

The authors declare that they have no conflict of interest.

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