

Cite this: *J. Mater. Chem. C*, 2022,  
10, 10853

## meso-Ethynyl-extended push–pull type porphyrins for near-infrared organic photodetectors†

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Natural porphyrins play a key role in a range of vital functions such as oxygen transport in the bloodstream and the conversion of light to chemical energy in plants. Likewise, synthetic porphyrin derivatives can be used to detect light and convert it into an electrical current in photodiodes. The versatility of porphyrinoid chemistry allows to extend the absorptivity (and hence detectivity) to the near-infrared while maintaining good solubility, suitable electrochemical properties, and compatibility with the electron acceptor molecules required to achieve a reasonable photocurrent. Here, our efforts on the design and synthesis of novel push–pull type meso-ethynyl-extended porphyrin compounds, both of A–D–A and D–A–D type (D = donor, A = acceptor), and their evaluation in prototype near-infrared organic photodetector devices are presented. The push–pull design with strongly electron-deficient building blocks results in absorption onsets up to 1200 nm, translating in an optical gap approaching 1 eV. Both A–D–A and D–A–D small molecules show good photodetector performance, with a peak specific detectivity near  $2 \times 10^{11}$  and  $4 \times 10^{11}$  Jones at 1000 nm (at  $-2$  V bias), respectively. These values are among the best reported so far for small molecule based near-infrared organic photodetectors.

Received 11th February 2022,  
Accepted 7th July 2022

DOI: 10.1039/d2tc00588c

rsc.li/materials-c

## Introduction

Modern applications are often nature-inspired, in the sense that we humans try to mimic a specific strategy adopted by nature.<sup>1</sup> An example is the ‘lotus effect’, referring to the self-cleaning properties of a surface as a result of the ultra-hydrophobicity as observed on lotus leaves.<sup>2</sup> The human sight presents another interesting example, for which we have invented the camera.<sup>3</sup> The sensitivity of our eyes is truly impressive and finds its origin in a sequence of complex chemical and physical processes. The chromophore interacting

with (visible) light is retinal. Upon photon absorption, the configuration of the retinal molecule is altered from the curved *cis* isomer to the straight *trans* isomer. This configurational change triggers a chemical cascade in the neighboring opsin protein that results in the perception of light or images in our brain.<sup>4</sup> Although the result is the same for man-made cameras (*i.e.* an image), the principle of capturing light and converting it into an image is fundamentally different. Whereas *cis–trans* isomerization occurs in retinal upon light absorption, man-made devices make use of semiconductors that generate free charges upon photon absorption (the ‘photovoltaic effect’). It has some similarities with the photoconversion process in green plants converting sunlight, *via* a series of electron transfer events, into a chemical potential and stored chemical energy. The active organic materials used in plants are chlorophyll molecules, which are porphyrin derivatives.<sup>5</sup> Therefore, it feels ‘natural’ to use porphyrin molecules as active materials for photovoltaic and photo-sensing applications as well.

Substituted porphyrin molecules are categorized as ‘small molecule’ chromophores. Compared to (conjugated) polymers, their size and molar mass is well defined, without notable batch-to-batch or end group variations.<sup>6,7</sup> This makes small molecules more attractive in terms of reproducible

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† Electronic supplementary information (ESI) available: Additional documentation on the synthesis and characterization of the meso-ethynyl-extended porphyrins and their precursors (strategy 1 and 2), as well as on the OPD device fabrication, characterization, and optimization, is available as supplementary information. See DOI: <https://doi.org/10.1039/d2tc00588c>

physicochemical and optoelectronic properties. Additionally, the conjugation length is strictly defined, resulting in more narrow absorption bands.<sup>8</sup> Consequently, the absorption edge is sharper and with that the energy loss in the photovoltaic process is reduced. On the other hand, the conjugated system is smaller as compared to polymers, which limits the optical gap. Nevertheless, reducing the bond-length alternation, enforcing molecular planarity, increasing the aromatic resonance energy or using the ‘strong donor-strong acceptor’ concept does allow to red-shift the absorption of molecular chromophores to a certain extent.<sup>9</sup> Nowadays, small organic molecules with an optical gap as low as 0.17 eV are known.<sup>10</sup> Nonetheless, the majority of near-infrared (NIR) photoactive organic semiconductors reported to date are polymer-based. In particular, the research performed on small molecule chromophores in the field of NIR organic photodetectors (OPDs) is limited to a handful of examples. In most cases, phthalocyanine or porphyrin derivatives have been used, but examples with squaraine, boron dipyrromethene (BODIPY), and indacene-dithiophene-benzothiadiazole-rhodanine (IDTBR) have been reported as well.<sup>11</sup> Quite often, NIR detectivity is claimed, but significant NIR absorption (above 900 nm) is only observed as tail absorption. In this respect, studies worth mentioning are the ones presented by M. Young *et al.*,<sup>12</sup> Z. Su *et al.*,<sup>13</sup> and J. Zimmerman *et al.*,<sup>14</sup> who used an organic heptamethine salt (in combination with C<sub>60</sub>), lead phthalocyanine (PbPc, with C<sub>70</sub>), or a porphyrin tape (with C<sub>60</sub>), respectively. The organic heptamethine (tetrafluoroborate) salt allowed to detect wavelengths as long as 1500 nm with a peak external quantum efficiency (EQE) of 2% at 1300 nm.<sup>12</sup> The PbPc:C<sub>70</sub> combination afforded a higher peak efficiency of 30% but only at 900 nm,<sup>13</sup> while the porphyrin tape generated 6.5% EQE at 1350 nm.<sup>14</sup> Therefore, it seems justified to state that NIR-photoactive small molecules are currently underexplored compared to polymeric variants.<sup>11,15–17</sup>

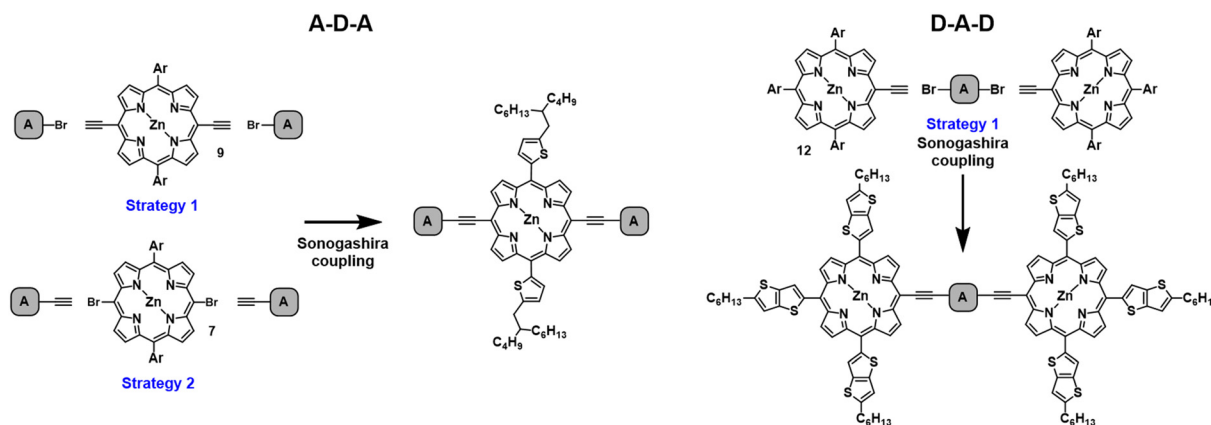
In this work, we investigate nature-inspired porphyrinoid semiconductors for their use in NIR OPDs. Red-shifting the absorption spectrum is enabled by the multiple chemical modifications possible on the porphyrin scaffold. The β- and

*meso*-positions can be varied and the porphyrinato ligand can be metalated, allowing a large structural degree of freedom to tune the porphyrinoid chromophore.<sup>18,19</sup> An interesting class of porphyrinoid materials, the *meso*-ethynyl-bridged acceptor-donor-acceptor (A-D-A) and donor-acceptor-donor (D-A-D) type porphyrins, with the porphyrin as the D part, allows the combination with electron acceptors of various strength to obtain a more red-shifted absorption.<sup>20,21</sup> So far, only one monomeric *meso*-ethynyl-extended A-D-A porphyrinoid material has been applied as a NIR OPD active material. In this report by L. Li *et al.*, the A part was a benzothiadiazole, which is known to have a modest acceptor strength, yielding an absorption onset of 950 nm.<sup>22</sup>

Here, the porphyrin (Por) donor part is combined with multiple acceptors of various strength in an A-D-A or D-A-D configuration. Combination with thieno[3,4-*b*]pyrazine (TP), thiadiazolo[3,4-*g*]quinoxaline (TQ), and benzobisthiadiazole (BBT) acceptors resulted in peak absorptions near 800, 950, and 1000 nm, respectively, for the A-D-A type molecules. In the case of the D-A-D materials, two different TQ moieties were combined with the porphyrin donor, yielding peak absorptions near 900 and 1000 nm. The TQ-Por-TQ and Por-TQ-Por molecules were blended with PC<sub>71</sub>BM and tested in OPD devices. Optimization of the solvent system, additive concentration, and solvent vapor annealing resulted in a maximum specific detectivity (*D*\*) of 4 × 10<sup>11</sup> Jones (at -2 V bias) at 1000 nm.

## Results and discussion

The vast number of possibilities to modify the porphyrin scaffold allows to fine-tune the final material properties in terms of solubility, spectral response, energy levels, and charge carrier mobility. In this work, only the four *meso*-positions have been substituted, of which two (for A-D-A) or three (for D-A-D) positions were used for attaching small alkylated aromatic moieties, primarily to increase the solubility according to the length and branching of the alkyl chains (Scheme 1). Besides, the small aromatic rings somewhat extend the chromophore (despite the torsion angles) and with that a slightly red-shifted



**Scheme 1** A<sub>2</sub>B<sub>2</sub>- and A<sub>3</sub>B-Zn(II)-porphyrin precursors required for the final Sonogashira cross-couplings to yield the envisioned A-D-A and D-A-D type end products. The alkyne moiety can be either on the porphyrin donor (strategy 1) or on the acceptor building block (strategy 2).

absorption is realized. The remaining *meso*-positions were used to link acceptor units with increasing strength, with the intention to shift the absorption spectrum into the NIR. The attachment of the acceptor units to the porphyrin core was done using ethynyl linkers to keep the molecular chromophores planar and therefore efficiently extend the conjugated system. Finally, it was opted to introduce Zn(II) as metal ion since solvent coordination to the Zn center has previously been shown to be advantageous for solution processing.<sup>18</sup>

The porphyrin materials targeted in this study are ethynyl-bridged *trans*-A<sub>2</sub>B<sub>2</sub>- and A<sub>3</sub>B-Zn(II)-porphyrins (Scheme 1). For the *trans*-A<sub>2</sub>B<sub>2</sub>-porphyrins, multiple synthetic routes are known to build the porphyrin core. The synthetic route chosen here is outlined in Scheme S1 (ESI<sup>†</sup>), affording the 5,15-bis(ethynyl)porphyrin precursor **9**.<sup>23</sup> Likewise, the monoalkynated A<sub>3</sub>B-porphyrin precursor **12** was synthesized starting from pyrrole, 5-hexylthieno[3,2-*b*]thiophene-2-carbaldehyde, and trimethylsilylcarbaldehyde, as shown in Scheme S2 (ESI<sup>†</sup>).<sup>24</sup> Upon Sonogashira cross-coupling with suitable acceptor moieties, these porphyrin cores should give access to the envisaged push-pull structures (Scheme 1, strategy 1).

The final Sonogashira cross-coupling between the porphyrin donor and the acceptors is also possible with the alkyne moiety positioned on the acceptor components (Scheme 1, strategy 2). It was shown before that this procedure reduces the amount of homocoupling (affording A-D-D-A type side products).<sup>25</sup> Therefore, this synthesis route was initially followed for the A-D-A type porphyrins with the aim to increase the yield of the desired product and to simplify purification. Different acceptor moieties of varying 'pull' character were considered and their synthesis was attempted (see Section 3 in the ESI<sup>†</sup>). Unfortunately, it turned out that the acceptor building blocks were either quite insoluble or cleavage of the trimethylsilyl protective group gave rather unstable products that degraded during the reaction and/or purification. To produce the intended porphyrin materials, the Sonogashira cross-coupling was attempted directly after the deprotection for one of the alkynated acceptor molecules (thienoisindigo (TII) **29**), without prior purification. From <sup>1</sup>H-NMR analysis, the deprotected TII-alkyne acceptor **32** was assessed to be relatively pure (Fig. S31, ESI<sup>†</sup>) and was hence coupled to the dibrominated porphyrin core **7** (Scheme S10, ESI<sup>†</sup>). Investigation of the crude reaction product after the Sonogashira reaction *via* matrix-assisted laser desorption-ionization – time of flight (MALDI-ToF) mass spectrometry (Fig. S32, ESI<sup>†</sup>) confirmed the formation of the intended A-D-A molecule, as well as multiple undesired (homocoupled) compounds. Sonogashira cross-coupling *via* this route thus still resulted in an entire range of products and a very low yield (<10%) of the desired A-D-A compound. For this reason, this strategy was abandoned and we redirected our attention to the synthesis protocol starting from the *meso*-ethynyl-substituted A<sub>2</sub>B<sub>2</sub>- and A<sub>3</sub>B-porphyrins **9** and **12** (strategy 1 in Scheme 1).

For this approach, four different monobrominated and two different dibrominated acceptor building blocks were synthesized (see Schemes S3 and S4, ESI<sup>†</sup>), as required for the A-D-A

and D-A-D type porphyrins, respectively (Scheme 1). From the building blocks used in the 'failed' strategy 2, thiadiazolo[3,4-*g*]quinoxaline, thieno[3,4-*b*]pyrazine, and benzobisthiadiazole were retained. In the final Sonogashira reactions, the stable alkynated A<sub>2</sub>B<sub>2</sub>- and A<sub>3</sub>B-porphyrin cores were combined with the brominated acceptors in a mixture of dry toluene and triethylamine under N<sub>2</sub> atmosphere to which Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and CuI were added (Schemes S5 and S6, ESI<sup>†</sup>). Typically, three reaction products were obtained, *i.e.* the desired A-D-A (D-A-D) compound, the expected homocoupled product A-D-D-A (D-A-A-D), and the debrominated acceptor molecule. In all cases, the desired A-D-A (D-A-D) material was the main product. Purification was performed *via* flash column chromatography followed by preparative (recycling) gel permeation chromatography to yield the six final *meso*-ethynyl-extended porphyrin products shown in Fig. 1. Structural characterization of the novel materials was done by <sup>1</sup>H-NMR spectroscopy and MALDI-ToF mass spectrometry. All data can be retrieved from the ESI<sup>†</sup>.

Analysis of the electrochemical and photophysical properties of the final compounds was performed by cyclic voltammetry (CV) and UV-VIS-NIR absorption spectroscopy (Fig. 2 and Table S1, ESI<sup>†</sup>). From the UV-VIS-NIR absorption spectra it can be concluded that the acceptor strength – increasing from the TP (**TP-Por-TP**) over the TQ (**R<sub>2</sub>TQ-Por-TQR<sub>2</sub>** and **TQ-Por-TQ**) to the BBT (**BBT-Por-BBT**) variant in case of the A-D-A type porphyrins, and from the 'naked' TQ variant (**Por-TQ<sub>n</sub>-Por**) to the thiophene-flanked TQ (**Por-TQ-Por**) for the D-A-D type porphyrins – indeed determines the red-shift observed for the intramolecular charge-transfer absorption band at low energy. Peak NIR absorptions (in film) were situated at 786, 919, 929, and 986 nm for **TP-Por-TP**, **R<sub>2</sub>TQ-Por-TQR<sub>2</sub>**, **TQ-Por-TQ**, and **BBT-Por-BBT**, and 873 and 948 nm for **Por-TQ<sub>n</sub>-Por** and **Por-TQ-Por**, respectively. Compared to the absorption spectra in solution (Fig. S11, ESI<sup>†</sup>), an additional red-shift of 130 nm was observed for **TQ-Por-TQ** and assigned to a strong stacking tendency. The π-π stacking behavior was also observed in the MALDI-ToF mass spectrum of the pure material (Fig. S6, ESI<sup>†</sup>), where two and even three closely interacting molecules bear a single charge. CV measurements (in film, Fig. S12, ESI<sup>†</sup>) confirmed the increasing acceptor strength trends as the electrochemical bandgap reduced from roughly 1.7 eV for **TP-Por-TP** to 1.5 eV for **R<sub>2</sub>TQ-Por-TQR<sub>2</sub>**, 1.2 for **TQ-Por-TQ**, and 1.0 eV for **BBT-Por-BBT**, and diminished from 1.3 eV for **Por-TQ<sub>n</sub>-Por** to 1.2 eV for **Por-TQ-Por** (Table S1, ESI<sup>†</sup>).

Although an optical and electrochemical characterization could be done for the six novel organic semiconductors, only **TQ-Por-TQ** and **Por-TQ-Por** were obtained in a sufficient quantity to allow full optimization in OPD devices. Fig. 2 shows the inverted device stack, ITO/ZnO:PEIE/Porphyrin:PC<sub>71</sub>BM/MoO<sub>3</sub>/Ag, employed for testing the porphyrin small molecules in OPDs. PC<sub>71</sub>BM was initially used as the electron acceptor in the bulk heterojunction blends. Device optimization was performed with the aim to enhance the light to dark current density ratio by varying the processing solvent, additives (and their concentration), and spin-coating speed. To further

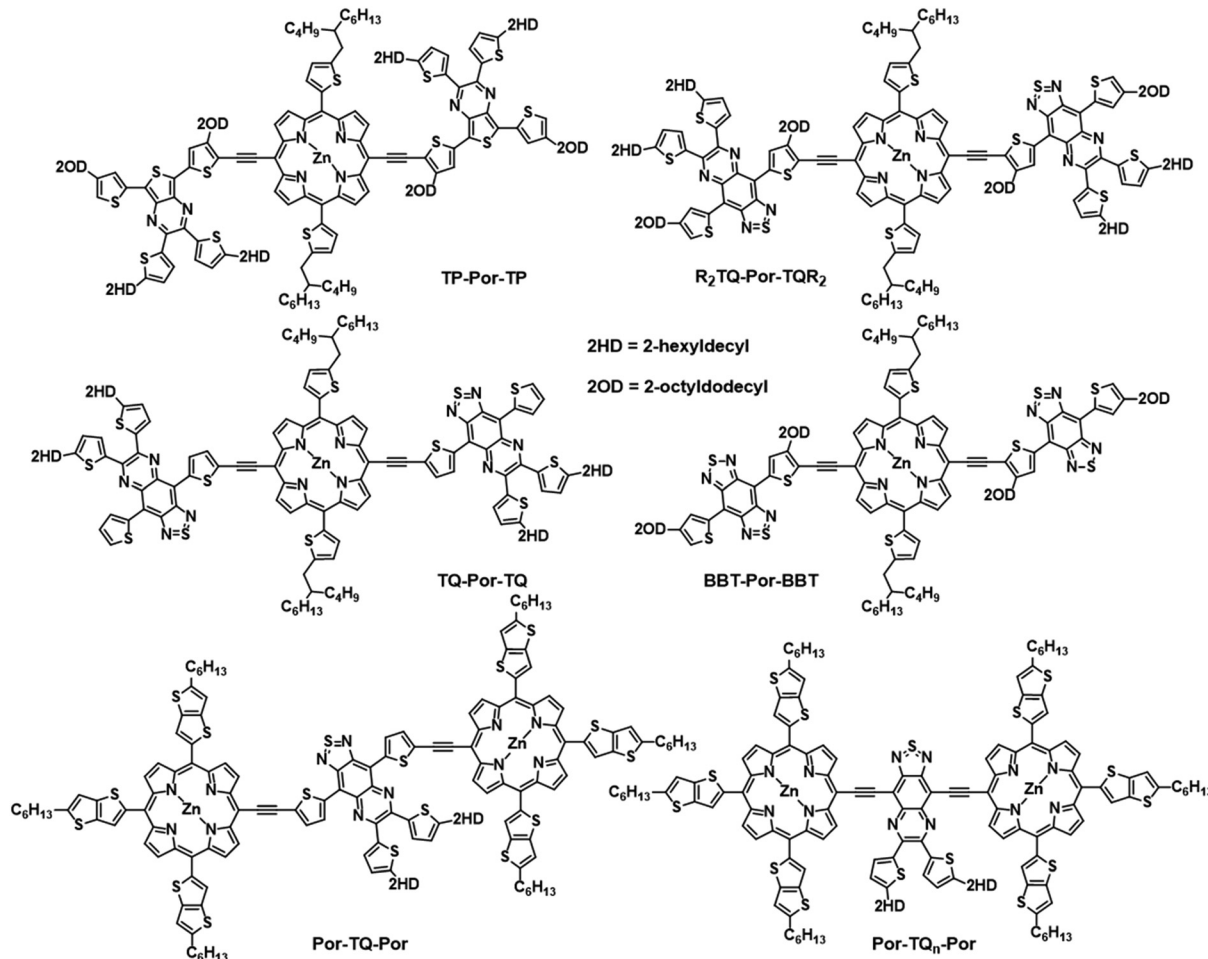


Fig. 1 Chemical structures of the six final *meso*-ethynyl-extended porphyrin chromophores.

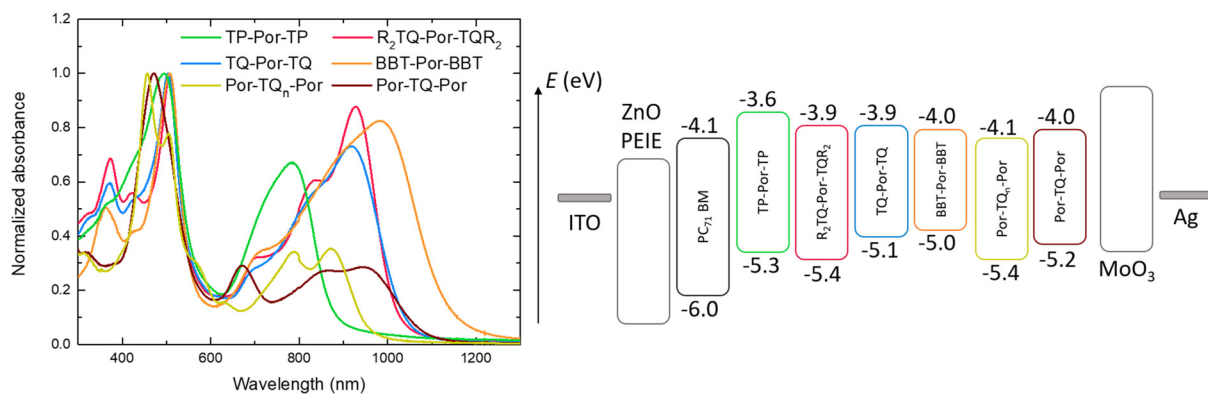
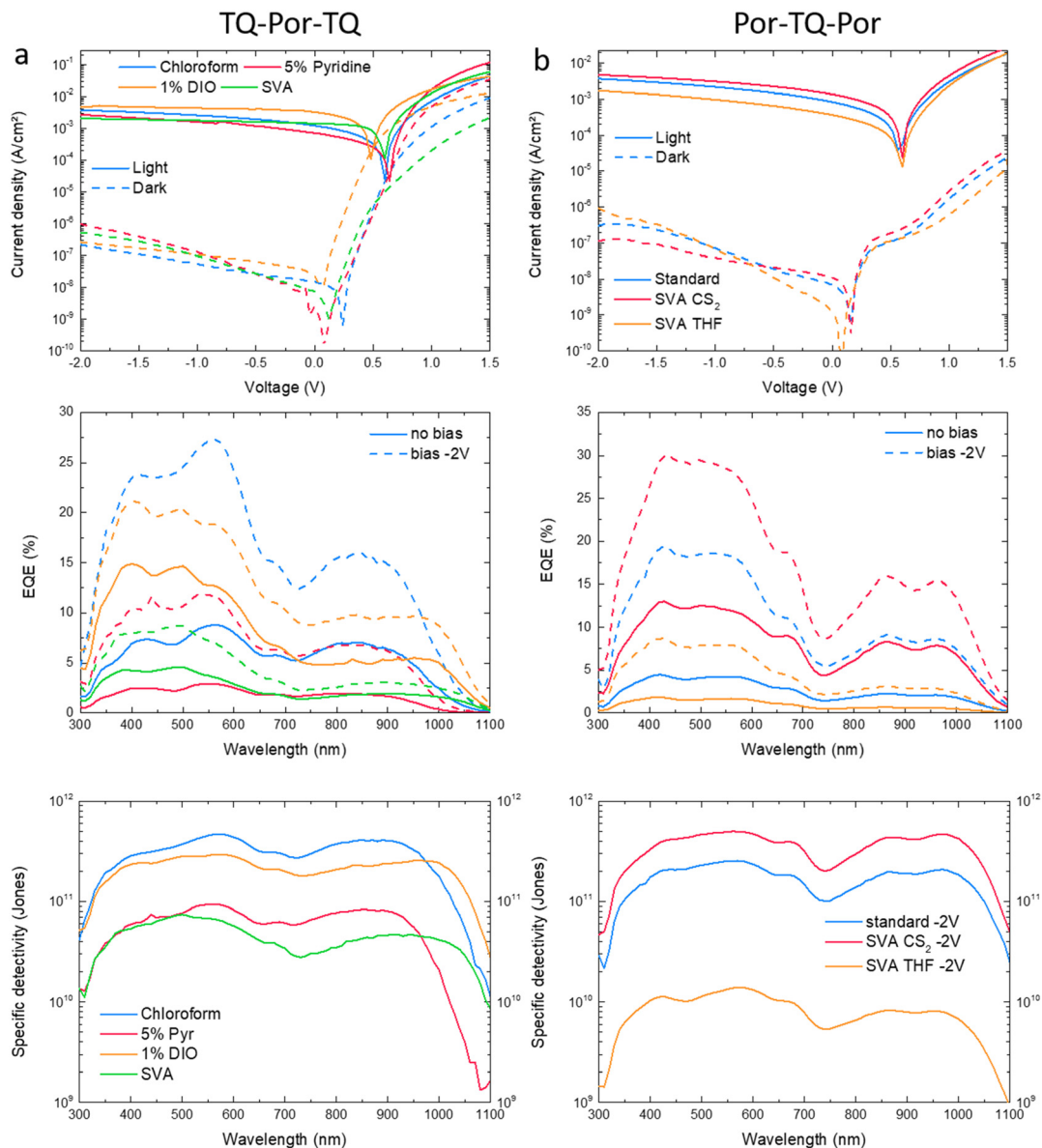


Fig. 2 Absorption spectra of the six neat porphyrin molecules (in film on glass) and energy level diagram displaying the HOMO–LUMO energy levels as derived from CV measurements (Table S1, ESI<sup>†</sup>) as well as the different layers used in the inverted OPD device stack.

optimize the active layer morphology, solvent vapor annealing (SVA) was applied. Details on the device optimization efforts are discussed in Section 2 of the (ESI<sup>†</sup>). Fig. 3(a) and (b) show the combined results ( $J$ - $V$ , EQE, and  $D^*$ ) of the different optimization steps performed for the **TQ-Por-TQ** and **Por-TQ-Por** based devices, respectively. The specific detectivity was determined

using the EQE measured at  $-2$  V and shot noise as the only contribution to the noise current, calculated from the dark currents at  $-2$  V (which is a good approximation according to our previous work<sup>26</sup>). For the **TQ-Por-TQ** devices, deposition from chloroform without additives or SVA yielded the best results, with detectivities up to  $4 \times 10^{11}$  Jones in the broad





**Fig. 3** (a)  $J$ - $V$ , EQE, and  $D^*$  overview for the different optimization efforts performed on the OPD devices prepared with a **TQ-Por-TQ**:PC<sub>71</sub>BM (1:2) active layer blend. Starting with chloroform as the casting solvent, pyridine and DIO were added in 5 and 1 v/v%, respectively, and finally SVA was performed (40  $\mu$ L THF for 120 seconds at 40  $^{\circ}$ C). (b)  $J$ - $V$ , EQE, and  $D^*$  overview for the different optimization efforts performed on the OPD devices prepared with a **Por-TQ-Por**:PC<sub>71</sub>BM (1:2) active layer blend. Starting with chlorobenzene as the casting solvent, pyridine and DIO were both added in 1 v/v%, respectively, followed by SVA (40  $\mu$ L THF or CS<sub>2</sub> for 50 seconds at 40  $^{\circ}$ C).

region from 500 to 900 nm (Fig. 3(a)). The use of 1,8-diiiodooctane (DIO; 1%) slightly lowered  $D^*$  to  $2 \times 10^{11}$  Jones but further broadened the spectral range to 1050 nm. Although the addition of pyridine (Pyr; 5%) as a solvent additive increased the open-circuit voltage ( $V_{OC}$ ) and SVA (40  $\mu$ L THF for 120 seconds at 40  $^{\circ}$ C) increased the fill factor (FF) of the photodiodes, both approaches resulted in an overall reduced  $D^*$  due to a lower EQE. For **Por-TQ-Por**, deposition from a chlorobenzene solution with 1 v/v% of DIO and Pyr, followed by SVA with CS<sub>2</sub>, resulted in a specific detectivity of  $4 \times 10^{11}$  Jones in the spectral region from 800 to 1000 nm (Fig. 3(b)). Other optimization trials failed to increase  $D^*$ . Preliminary  $J$ - $V$  results

for the **R<sub>2</sub>TQ-Por-TQR<sub>2</sub>**, **BBT-Por-BBT**, and **Por-TQ<sub>n</sub>-Por** blends with PC<sub>71</sub>BM are shown in Fig. S17 (ESI<sup>†</sup>). For the **R<sub>2</sub>TQ-Por-TQR<sub>2</sub>** and **BBT-Por-BBT** based devices, overall low light current densities were obtained, while in the case of **Por-TQ<sub>n</sub>-Por** a rather high dark current was observed. Additive optimization was performed to a minimal extent, but did not afford significant improvements in device performance.

To further analyze the effects of the device optimization efforts, active layer morphology and response speed studies were conducted. Fig. S18 (ESI<sup>†</sup>) shows the topography of the **TQ-Por-TQ** and **Por-TQ-Por** based blends after processing optimization as obtained by atomic force microscopy (AFM). From

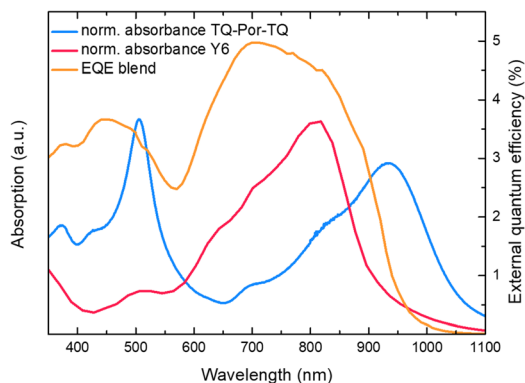


Fig. 4 Overlay of the absorption spectra of neat **TQ-Por-TQ** and **Y6** (both in film) and the EQE spectrum of the photodiode prepared from the 1:1 blend.

these images it can clearly be seen that the optimized blends show an intimate mixing, both for the **TQ-Por-TQ** and **Por-TQ-Por** bulk heterojunctions. For the blends with the **R<sub>2</sub>TQ-Por-TQR<sub>2</sub>** and **BBT-Por-BBT** donor porphyrins, significant phase separation was observed (Fig. S19, ESI<sup>†</sup>), explaining the poor charge generation under light conditions. Grazing-incidence wide angle X-ray scattering (GIWAXS) was performed on the optimized blends of **TQ-Por-TQ** and **Por-TQ-Por** to examine the structural differences between the two material systems. In Fig. S20 (ESI<sup>†</sup>) it can be seen that **Por-TQ-Por** exhibits signs of crystalline order, with sharp diffraction peaks which are attributed to the small molecule phase. Meanwhile, the scattering for the **TQ-Por-TQ** blend is more isotropic with broader scattering peaks, likely due to the presence of an excess of branched side chains which impede ordering in the lamellar direction.

Rise ( $t_r$ ) and fall ( $t_f$ ) times were determined for the optimized **TQ-Por-TQ** and **Por-TQ-Por** based OPD devices. The  $t_r$  and  $t_f$  were calculated from the measurements as depicted in Fig. S21 (ESI<sup>†</sup>). LED light ( $\lambda = 450$  nm), pulsed with a frequency of 123 Hz, was used to illuminate the devices. The time needed to get the photocurrent signal from 10 to 90% ( $t_r$ ) corresponds to 435 and 556  $\mu$ s for the **TQ-Por-TQ** and **Por-TQ-Por** base OPDs, respectively, while the fall times from 90 to 10% ( $t_f$ ) are 457 and 963  $\mu$ s, respectively.

In a final experiment, **PC<sub>71</sub>BM** was exchanged for 6 different commercially available non-fullerene acceptors (NFAs; structures shown in Fig. S22, ESI<sup>†</sup>) for the combination with **TQ-Por-TQ**. These NFAs have been shown to significantly increase the performance of bulk heterojunction blends, as shown throughout the OPV field in the past years.<sup>27</sup> An even more interesting property of NFAs, specifically for NIR OPDs, is their capability to be tuned toward NIR absorption. This can boost the EQE in the NIR region and ultimately increase the sensitivity. A general trend we observed for these NFA-containing OPD devices was the low dark current density ( $J_D$ ), in the order of 10 nA cm<sup>-2</sup>, but unfortunately also low photocurrent density ( $J_{ph}$ ), below 1 mA cm<sup>-2</sup> at -2 V bias (under AM1.5G solar illumination, 100 mW cm<sup>-2</sup>; Fig. S23, ESI<sup>†</sup>). An exception was the device based on the **TQ-Por-TQ:Y6** blend, yielding 3 mA cm<sup>-2</sup> at -2 V

bias. Unfortunately, the EQE spectrum suggests that **TQ-Por-TQ** barely contributes to the photocurrent. Fig. 4 clearly shows the mismatch of the **TQ-Por-TQ** absorption and the EQE spectrum.<sup>28</sup> A clearly unfavorable blend morphology, as indicated by AFM (Fig. S24, ESI<sup>†</sup>), is likely at the origin of these poor results.

## Conclusions

Six new *meso*-ethynyl-extended A-D-A and D-A-D-type porphyrin molecules were successfully synthesized. Depending on the acceptor strength, NIR-sensitive small molecules were obtained with a maximum absorption onset up to 1200 nm. Prototype photodetectors prepared from **TQ-Por-TQ** or **Por-TQ-Por**:**PC<sub>71</sub>BM** (1:2) blends were optimized in terms of casting solvent, additive concentration, and solvent vapor annealing. This resulted in peak specific detectivities near  $2 \times 10^{11}$  and  $4 \times 10^{11}$  Jones at 1000 nm (at -2 V bias) for the **TQ-Por-TQ** and **Por-TQ-Por** based photodiodes, respectively. Additionally, six non-fullerene acceptors were tested in combination with the **TQ-Por-TQ** donor. Unfortunately, these devices yielded poor light currents and consequently poor external quantum efficiencies. However, as this is only the second report on *meso*-ethynyl-extended porphyrins for near-infrared organic photodetectors, there is certainly room for further investigations and improvements. Alternatively, **TQ-Por-TQ** could be used in ternary blends to red-shift the absorption and benefit from a well-performing blend combination for sensitive light detection. As multiple promising examples are shown nowadays in both the organic photodetector and solar cell field,<sup>29-33</sup> future work could be in this direction.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

S. G., S. B., and J. V. acknowledge the Research Foundation – Flanders (FWO Vlaanderen) for their PhD fellowships. J. V. also acknowledges funding by FWO Vlaanderen (V413722N) and a personal grant from the District 1630 of Rotary International, supported by the Rotary foundation, allowing a student researcher visit at Stanford University. T. J. Q. acknowledges support from the National Science Foundation Graduate Research Fellowship Program under grant DGE-1656518. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists, Office of Science Graduate Student Research (SCGSR) program. The SCGSR program is administered by the Oak Ridge Institute for Science and Education for the DOE under contract number DE-SC0014664. Use of the Stanford Synchrotron Radiation Light source, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under

Contract No. DE-AC02-76SF00515. Part of this work was performed at the Stanford Nano Shared Facilities (SNSF), supported by the National Science Foundation under award ECCS-2026822. The authors gratefully acknowledge Prof. Alberto Salleo for his support. K. V. and W. M. are grateful for project funding by the FWO (G0D0118N, G0B2718N, GOH3816NAUHL, and I006320N). Hasselt University and IMOMEC have been partners in the SBO project MIRIS (Monolithic Infrared Image Sensors), supported by VLAIO (Vlaams Agentschap Innoveren en Ondernemen). V. C. thanks the Ministerio de Educación, Cultura y Deporte of Spain for an FPU grant (FPU15/02170). F. L. and P. C. are grateful for project funding by MCI (Spain) (PID2019-105049RB-I00) and MICIU (RED2018-102815-T).

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