A Renaissance of Color: New Structures and Building Blocks for Organic Electronics

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ABSTRACT: Natural dyes and pigments like indigo and its derivatives valued for their bright colors and photochemical stability has been used since antiquity. Recently, the need for better performing materials in the organic electronics field has inspired a resurgence of these historical molecules and their subsequent transformation into new families of π -conjugated building blocks used to construct new (macro)molecular semiconductors. This *Highlight* will explore the renaissance of notable building blocks including diketopyrrolopyrrole, (iso)indigo, benzodipyrrolidone, and benzodifuranone, as well as nonfullerene acceptor structures 9,9'-bifluorenylidene and quinacridone. In addition, as the organic electronics field continues to evolve, the design of molecules with precise structure and function embodies a new paradigm for the next generation of materials. Representative examples will be described that embrace this new model and point the direction for advanced technologies. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem **2013**, *51*, 1263–1271

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INTRODUCTION Natural dyes and pigments have been prized for thousands of years. In ancient Europe, precursors to expensive and brightly colored pigments used to color textiles for the royal and elite social classes were painstakingly extracted from marine invertebrates. One such pigment famously known as Tyrian purple was derived from the Mediterranean sea snail Bolinus brandaris and has been used since the 13th Century BCE.¹ According to Greek mythology, Tyrian purple was discovered as Heracles, accompanied by his dog and his beloved nymph Tyrus, strolled along the shores of Phoenicia. The dog, having devoured a nearby snail, returned with its mouth stained a brilliant purple and captivated by the sight, Tyrus demanded a robe cloaked in the magnificent color. Although the details of its discovery will likely never be known, this celebrated pigment was determined to be comprised primarily of the chemical 6,6'dibromoindigo by the German chemist Friedländer^{2,3} in 1909 (for structure, see Fig. 1).

Industrialization and the advent of modern synthetic organic chemistry beginning in the late 19th Century dramatically reduced the cost and increased availability of important colorants. Today, many of these dyes and pigments have found new purpose in the flourishing field of organic electronics research. This revival is driven by a need for materials that combine good optical absorption, mechanical, and charge transport properties with solution processability and stability, particularly for organic photovoltaic (OPV) applications.⁴ As a result, a variety of π -conjugated organic molecules that absorb light strongly in the visible region of the electromagnetic spectrum are now important building blocks used to construct semiconducting (macro)molecules with attractive properties for use in organic electronic devices.^{5,6}

The rapidly progressing field of organic electronics research has led to a renaissance in the chemistry of dye molecules, compelling scientists to revitalize old pigments, transform them into soluble dyes, and apply them in the construction of new and complex semiconducting materials. This Highlight will explore the resurgence of notable building blocks including diketopyrrolopyrrole (DPP), (iso)indigo, benzodipyrrolidone, and benzodifuranone, as well as nonfullerene acceptor structures 9,9'-bifluorenylidene (99BF) and quinacridone. Additionally, as the field continues to evolve, there is an emerging trend that frames the future of successful organic electronics, and particularly, OPV research. The "mix and match" approach to (macro)molecular discovery by rudimentarily combining different building blocks to generate new (polymeric) structures is being replaced by the meticulous design of molecules with precise structure and function.

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Fulvio G. Brunetti received his Ph.D. from the University of Trieste (Italy) in 2008 under the supervision of Professor Maurizio Prato. He then moved to the University of California, Santa Barbara (UCSB) as postdoctoral fellow in the group of Professor Fred Wudl, studying accepting systems for bulk heterojunction solar cells. After a year at IMDEA Institute (Spain) as a Juan de la Cierva researcher, he returned to UCSB in the group of Professor Craig Hawker where he is currently working on organic thermoelectric materials. His interest is focused on the design and synthesis of new materials for applications in organic electronics.

Craig J. Hawker was born in 1964 in Toowoomba, Australia and is currently the Director of the Materials Research Laboratory at the University of California, Santa Barbara where he is also a Professor in the Materials, Chemistry, and Biochemistry departments. After undergraduate education at the University of Queensland, he completed a Ph.D. in 1988 at Cambridge University (supervisor Professor A. R. Battersby). Shifting to the world of polymer chemistry, he undertook a post-doctoral fellowship with Professor Jean Frèchet at Cornell University from 1988 to 1990 and then returned to the University of Queensland as a Queen Elizabeth II Fellow from 1991 to 1993 before spending 12 years as a research staff member at the IBM Almaden Research Center. His research has focused on the interface between organic and polymer chemistry with emphasis on the design, synthesis, and application of well-defined macromolecular structures in biotechnology, microelectronics, and surface science.

> Representative examples will be described that embrace this new model and point the direction for advanced technologies.

INDIGO AND ISOINDIGO

Much like the halogenated derivative and primary constituent of Tyrian purple, indigo has been used as a textile pigment for thousands of years. Natural indigo is obtained from the plants Indigofera tinctoria and Isatis tinctoria which contain a glucoside called indican. Enzymatic hydrolysis of the glucose residue produces indoxyl, which spontaneously dimerizes and oxidizes in air to provide indigo. The cultivation of indican-producing plants occupied a land area of nearly 7000 km² (larger than the state of Delaware) prior to the commercialization and large-scale production of synthetic indigo by BASF in 1897. Although now almost entirely artificial, indigo is still the

Vitale in Ravenna, Italy (6th Century CE).

FIGURE 1 Left, molecular structure and model of 6,6'-dibro-

moindigo. This chemical is the primary constituent of Tyrian

purple, a pigment used since the 13th Century BCE. Right,

mosaic of Byzantine Emperor Justinian the Great shown wearing a robe dyed with Tyrian purple located in the Basilica of St.









FIGURE 2 (a) Image of an ambipolar transistor fabricated using indigo and (b) cyclic voltammograms of indigo and 6,6'-dibromoindigo thin films. The indigoid structures are shown; (*E*)-stereoisomers are stabilized by intramolecular hydrogen bonding.^{8,9} Copyright 2012 Wiley-VCH.



largest produced textile dye in the world with an annual production of thousands of tons—enough to manufacture over two billion pairs of blue jeans.^{7,8}

Researchers have recently explored the promise of these historical pigments in the organic electronics field by successfully employing indigo as the semiconducting material in high-performance organic field effect transistors (OFETs) (Fig. 2). Sariciftci and coworkers⁹ demonstrated that indigo-based OFET devices display outstanding properties including ambipolar charge transport and well-balanced electron and hole mobilities of approximately 0.01 cm² V⁻¹ s⁻¹. The highly ordered crystalline structure of indigo in the solid state coupled with reversible redox properties leads to impressive charge transport and ambipolar characteristics. In an alternate study, these researchers demonstrated that 6,6'-dibromoindigo (the primary constituent of Tyrian purple) is also an effective semiconductor, producing OFET devices with electron and hole mobilities of 0.22 and 0.03 cm² V⁻¹ s⁻¹, respectively.¹⁰ This study suggests that natural materials could play an important role in the future development of sustainable electronic devices.

Despite these recent successes in unique transistor devices, indigo does not possess the characteristics of a good building block owing to its discontinuous π -conjugation and thus its widespread application in materials for organic electronics is limited. However, its structural isomer isoindigo, which has also been used previously in the dye industry, has many desirable attributes that have made it the subject of recent investigations. The unique structure of isoindigo imparts a strong electron withdrawing character owing to conjugation of the lactam rings in conjunction with an extended delocalized π system throughout the bis-oxindole framework. The advantageous properties of isoindigo were first utilized by Reynolds and coworkers¹¹ in 2010 for the preparation of a well-defined oligomer 1 with a donor/acceptor/donor (D/A/ D) architecture for OPV applications (for structures incorporating the isoindigo building block, see Fig. 3). Broad visible light absorption ($E_g = 1.76$ eV) and reversible oxidation and reduction characteristics allow bulk heterojunction (BHJ) solar cells to be fabricated using the D/A/D oligomer as donor and PC₆₁BM as acceptor. Significantly, a power conversion efficiency (PCE) up to 1.76% with an open circuit voltage (V_{oc}) of 0.74 V was observed. Further refinement of the processing conditions including use of alternative solvent additives (e.g., polydimethylsiloxane) resulted in an increase in PCE to nearly 3.7%.12



FIGURE 3 Structures of oligomers and polymers containing the isoindigo building block and its derivatives used in organic solar cell and OFET devices.



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FIGURE 4 Structures of donor/acceptor copolymers prepared using the DPP building block as an electron-deficient unit.

Inspired by the unique characteristics of isoindigo, Wang and Andersson¹³ synthesized a low band gap polymer **2** $(E_{\rm g} = 1.6 \text{ eV})$ with alternating thiophene and isoindigo units. Solar cells fabricated using this polymer and PC₇₁BM exhibited a PCE of 3.0% and high $V_{\rm oc}$ of 0.89 V. Refining this structure, a narrow bandgap D/A copolymer **3** based on terthiophene and isoindigo repeat units was prepared and solar cell devices fabricated using this polymer and PC₇₁BM demonstrated a markedly improved PCE of 6.3% owing to appropriate frontier energy level alignment and good optical absorption properties.¹⁴ These investigations demonstrate the promise of isoindigo as an electron-deficient building block for the construction of new conjugated polymers.

Like its structural isomer, isoindigo-based materials have also established an impressive reputation in OFET devices. Pei and coworkers¹⁵ prepared a variety of narrow bandgap D/A copolymers utilizing isoindigo in combination with different donor units and investigated their field-effect mobilities. Copolymer 4 incorporating a bithiophene donor unit displayed an impressive maximum hole mobility of 1.06 cm² V^{-1} s⁻¹. Furthermore, the polymers exhibited excellent environmental stability owing to their low-lying highest occupied molecular orbital (HOMO) energy levels. Switching the electronic role of isoindigo, a new thiophene analogue was recently reported by Ashraf et al.¹⁶ and used as a donor unit in conjunction with the common acceptor benzothiadiazole to construct ultra-narrow bandgap D/A copolymers. Polymer **5** exhibits an absorption maximum around 1050 nm ($E_{\rm g}$ = 0.92 eV), and low-lying LUMO energy levels promote excellent ambipolar behavior in OFET devices with both hole and electron mobilities recorded more than 0.1 cm² V⁻¹ s⁻¹.

DIKETOPYRROLOPYRROLE

Another successful building block for organic electronic materials that has gained significant interest in recent years is 3,6diaryl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione, commonly referred to as DPP. Similar to the indigoid structures discussed previously, DPP was first developed as a high-performance industrial pigment for paints, plastics, and inks.^{17,18}



The diphenyl derivative was the first DPP architecture to be reported by Farnum et al.¹⁹ in 1974 with the DPP core architecture having a number of characteristics that make it an ideal building block for organic electronic materials including strong visible light absorption, good photochemical stability, and an extended π -conjugated framework.²⁰ Additionally, the accessibility of the lactam nitrogens for chemical functionalization provides a versatile handle for altering physical properties such as solubility and solid-state ordering.²¹

The first conjugated polymer containing the DPP unit synthesized for OPV applications was reported by Janssen and coworkers²² in 2008 (for polymer structures containing the DPP building block, see Fig. 4). Polymer 6 was constructed using a DPP derivative containing 2,5-dithienyl aromatic groups as an electron-deficient unit with bithiophene donor segments, leading to a narrow optical bandgap of 1.4 eV as well as a strong tendency to aggregate. Solar cell devices fabricated using this polymer and PC71BM demonstrated a PCE of 4.0% with a $V_{\rm oc}$ of 0.61 V. More recent research with DPP has demonstrated the synthetic advantages arising from the functionalizable lactam nitrogens. Increasing the solubilizing ability of the substituents on the DPP unit allows for a greater range of donor units to be explored while maintaining processability. For example, polymer 7 replaces the alkylated bithiophene donor in 6 with a single thiophene unit and introduces a branched 2-hexyldecyl alkyl chain onto the DPP core to improve solubility behavior.²³ The polymer



FIGURE 5 Structures of well-defined p-type (10-13) and n-type (14) oligomeric semiconductors designed for organic solar cell applications.

exhibits a smaller bandgap of 1.3 eV in the solid state with balanced hole and electron mobilities of 0.04 and 0.01 cm² V⁻¹ s⁻¹, respectively, and provided solar cells fabricated using PC₇₁BM with an improved PCE of 4.7%.

The properties of the DPP building block can be readily adjusted by varying the aromatic substituents at the 2,5-positions of the DPP core. In 2010, Frèchet and coworkers²⁴ reported the synthesis of a refined narrow bandgap polymer 8 that employed a 2,5-difuryl-substituted DPP building block. The polymer was analogous to 7, but exchanged the two thiophene units that flanked the DPP core with furan heterocycles. Remarkably, incorporation of furan into the polymer backbone was shown to significantly increase the solubility of the polymer, allowing for smaller 2-ethylhexyl alkyl substituents on the DPP units to be employed. Solar cell devices fabricated with this polymer and PC71BM also achieved an increased PCE of 5.0%. Similarly, Bronstein et al.25 investigated a semiconducting polymer 9 incorporating a thieno[3,2-b]thiophene-substituted DPP building block as the electron-deficient unit. The thienothiophene units were shown to enhance the planarity of the polymer and promote a greater delocalization of the HOMO along the π -conjugated backbone. The backbone design inherent in 9 enhances intermolecular charge transport, resulting in an impressive maximum hole mobility of 1.95 $\text{cm}^2 \text{ V}^{-1}$ s^{-1} and a further increased PCE of 5.4% in solar cells fabricated using $PC_{71}BM$ as acceptor.

Although semiconducting polymers offer many advantages such as good film-forming capabilities, emerging research demonstrates that small molecules and well-defined oligomers are enticing structures for advancing the organic electronics field. These materials generally provide good solubility properties and benefit from facile purification and reproducible syntheses in contrast to their polymeric counterparts. Further reinforcing its utility as an important building block, DPP has also been used extensively in the construction of interesting small molecule and oligomeric semiconductors for OPV applications (Fig. 5).

Nguyen and coworkers²⁶ reported a D/A/D oligomer **10** based on a 2,5-dithieno-DPP building block containing terminal bithiophene donor units for use in BHJ solar cells. The D/A/D structure results in strong optical absorption (onset around 820 nm in thin films) with nanoscale ordering and fiber-like morphology observed by atomic force microscopy (AFM). Solar cell devices prepared using oligomer **10** containing *N*-2-ethylhexyl solubilizing groups with PC₇₁BM exhibited a PCE of 3.0%.²⁷ These researchers later designed a modified DPP-based small molecule **11** containing benzofuran terminal donor units.²⁸ This structural modification leads to a deeper HOMO energy level which was reflected in a high $V_{\rm oc}$ of 0.92 V in solar cell devices with PC₇₁BM providing a PCE of 4.4%.

Replicating this basic strategy, Frèchet and coworkers²⁹ introduced pyrene as a terminal donor unit to realize DPPbased oligomer **12**. The pyrene end-groups resulted in tight, crystalline packing influenced by strong intermolecular π - π interactions which was confirmed by X-ray diffraction studies (Fig. 6). The favorable molecular ordering led to solar cells incorporating PC₇₁BM as acceptor with PCE of 4.1% and a fill factor of approximately 0.6, one of the highest reported for small-molecule-based BHJ devices. An alternative A/D/A architecture was employed by Marks and coworkers³⁰ who employed a naphthadithiophene donor unit in the core of a new oligomer **13** with DPP terminal groups. Similarly, highly ordered molecular packing was observed affording high hole





FIGURE 6 The single crystal structure of DPP-oligomer **12** containing pyrene terminal units, demonstrating strong intermolecular π - π stacking interactions.²⁹ Copyright 2011 Wiley-VCH.

mobilities and resulting in solar cells with a PCE exceeding 4% using $PC_{61}BM$ as the acceptor.

In contrast to the hole-conducting (p-type) materials explored so far, the DPP building block has also been utilized for the construction of electron-conducting (n-type) materials. A new acceptor material **14** synthesized by Morin and coworkers³¹ combines many of the advantageous properties of the DPP unit with fullerenes. Attachment of 2,5-dithieno-DPP to C₆₀ via a conjugated ethynyl bridge resulted in a new DPP-fullerene dyad with increased solubility, improved visible light absorption, and altered optoelectronic properties including a higher LUMO energy which should lead to an increased $V_{\rm oc}$ in OPV devices. Several other DPP-based fullerene dyads and triads have also been prepared recently for use as active materials in BHJ solar cells.^{32,33}

BENZODIPYRROLIDONE AND BENZODIFURANONE

Continuing with the theme of developing building blocks based on older chemistry, benzodipyrrolidone and benzodifuranone are two recently rediscovered molecules with origins in the late 20th Century textile industry. These molecules were first developed by Imperial Chemical Industries beginning in the mid-1970s and commercialized as disperse dyes owing to their brilliant color and high photochemical stability.^{34,35} In analogy with DPP, these structures have now found new utility as conjugated building blocks for the construction of organic semiconducting materials (for polymer structures, see Fig. 7).



Benzodipyrrolidone can be described as an "elongated" DPP structure, wherein the two electron withdrawing lactam groups are fused to a central benzene ring. The planar benzodipyrrolidone core framework is synthesized in three steps starting from *p*-phenylenediamine and the final oxidation step ensures conjugation of the quinodimethane structure. Wudl and coworkers³⁶ recently synthesized a soluble derivative of benzodipyrrolidone containing N-2-octyldodecyl side chains and incorporated this new building block into D/A copolymers as an electron-deficient unit. Polymers 15 and 16 comprising both thiophene and phenyl donor units, respectively, were prepared by Suzuki crosscoupling and their transport properties were investigated. Polymer 15 revealed an ambipolar behavior with electron and hole mobilities of 6.4 \times 10⁻³ and 3.5 \times 10⁻³ cm² V⁻¹ s⁻¹, respectively, an optical absorption edge at 737 nm in the solid state ($E_g = 1.68$ eV), and a LUMO energy of -3.50 eV. Despite a lower molecular weight and limited conjugation through the biphenyl junction, polymer 16 also demonstrated strong n-type behavior and an interesting electron mobility of 2.4 \times 10⁻³ cm² V⁻¹ s⁻¹, close to that of PCBM.³⁷

In a similar fashion benzodifuranone, the lactone analogue of benzodipyrrolidone was recently employed as a building block in the synthesis of narrow bandgap D/A copolymers. Zhang and Tieke³⁸ prepared polymers **17** and **18** incorporating fluorene and thiophene donor groups, respectively, with a benzodifuranone derivative as the electron-deficient unit. Interestingly, the synthetic procedure reported for this benzodifuranone monomer provided asymmetrically substituted derivatives in high yield which conferred higher solubility and significant polarity to the materials along with the possibility to fine-tune electronic properties. The polymers exhibit broad optical absorption characteristics with extinction coefficients as high as 32,500 L mol⁻¹ cm⁻¹ and electrochemical bandgaps as low as 1.10 eV for **18**. Surprisingly, materials based on either benzodipyrrolidone and benzodifuranone



FIGURE 7 Structures of donor/acceptor copolymer prepared using the benzodipyrrolidone and benzodifuranone building blocks.



FIGURE 8 Structure of soluble malononitrile quinacridone derivative **19** and 99BF derivative **20** designed as new n-type small-molecule acceptor materials for OPV.

building blocks have not yet been investigated in OPV applications despite their promising optoelectronic properties.

QUINACRIDONE AND 99BF



The need for higher performing electron-accepting materials for photovoltaic applications has challenged synthetic chemists to find new n-type small molecules. Despite recent successes in the preparation of higher performance fullerene derivatives including, for example, indene- C_{60} bisadducts,³⁹ PCBM is still the most widely used acceptor in BHJ solar cells.⁴⁰ However, in contrast to the vast body of research dedicated to discovering new p-type semiconductors, relatively limited work has been performed on new nonfullerene acceptors. Recent reports have identified a number of nonfullerene acceptors for OPV applications of which two compelling examples include derivatives of quinacridone and 99BF (Fig. 8); it should be no surprise that both of these structures have been known for decades.

Quinacridone is a high-performance pigment used in paints and inks that was first synthesized in the early 20th Century.⁴¹ In 2011, Kang and coworkers⁴² reported a malononitrile derivative of quinacridone **19** with strong electron-withdrawing character and improved solubility imparted by solubilizing alkyl groups as a new acceptor material for organic solar cells. Quinacridone **19** displays significantly enhanced visible light absorption compared to PCBM while demonstrating similar frontier energy levels with the HOMO and lowest unoccupied molecular orbital (LUMO) energies measured to be -5.8 and -4.0 eV, respectively. Interestingly, the performance of the quinacridone derivative **19** in OPV devices employing poly(3-hexylthiophene) (P3HT) as a donor material was demonstrated to be highly dependent on the length of the alkyl side chain. A moderate PCE of 1.6% was achieved with the *N*-dioctyl derivative; however, reducing the chain length to dihexyl and dibutyl resulted in devices with significantly reduced performance. Additionally, quinacridone derivatives have also been employed in organic light-emitting diodes and BHJ devices as electron injection layers, enhancing luminance efficiency and PCE, respectively.^{43,44}

99BF has been studied since as early as 1963;⁴⁵ however, its unusual electronic properties have only recently been applied to organic semiconductor research. The overcrowded polycyclic structure can be envisioned simply as the dimer of two fluorene units connected through a double bond. Interestingly, 99BF does not exhibit typical electron-accepting features as it is devoid of electron-withdrawing substituents. However, steric interactions cause each fluorene fragment to twist by an angle of approximately 40° .⁴⁶ This twist strain is relieved upon reduction which leads to the formation of a radical anion that is stabilized by a 14-electron π -aromatic system. Wudl and coworkers⁴⁷ investigated the performance of 99BF derivative 20 as an acceptor material in solar cell devices using P3HT as the donor. Notably, a $V_{\rm oc}$ of 1.1 eV was obtained for the system, a value approximately double that of PCBM owing to the higher LUMO energy. Surprisingly, 99BF and its derivatives were used in the past as donors for the formation of donor-acceptor complexes^{46,48} with ambipolar behavior⁴⁹ being aided by the formation of electrochemically stable antiaromatic radical cations.⁵⁰

OUTLOOK

As the organic electronics field continues to evolve, it is becoming increasingly apparent that a paradigm shift is



FIGURE 9 (a) Molecular structure of DTS(TTh₂)₂ **21** used as a welldefined donor material with PC₇₁BM to prepare BHJ solar cells with a PCE of 6.7%. (b) Ultraviolet–visible absorption spectra of **21** in solution and thin film and (c) JV curves illustrating enhancement of device efficiency using a small amount of DIO processing additive.⁵³ Copyright 2012 Macmillan Publishers Limited.





FIGURE 10 (a) Structure of a contorted hexabenzocoronene 6-DBTTC **22** that forms hole-transporting columnar nanostructures upon thermal annealing. (b) Illustration of hole-transporting columns; (c) fluorescence micrograph, and (d) noncontact AFM image with cross-sectional profile, demonstrating a three-dimensional network of cables.⁵⁷ Copyright 2010 Wiley-VCH.

occurring in the way new organic semiconducting materials are designed. The "mix-and-match" approach of simply combining different building blocks to generate new (macro)molecules is quickly being replaced by a movement to build elaborate, designer molecules with precise structure and function. The rapidly growing research area of small-molecule-based organic electronics is a fitting example of how synthetic chemists have embraced this emerging ideology.^{51,52} This is not to say that the building blocks developed previously (or even those discussed in this highlight) have become obsolete; rather, they are being used more effectively than ever to construct sophisticated and precisely engineered molecular structures with unsurpassed properties and performance in organic electronic devices.

A seminal report by Bazan and coworkers recently demonstrated that record solar cell efficiency of 6.7% could be achieved using a meticulously designed narrow bandgap small molecule donor in combination with PC₇₁BM.⁵³ The researchers designed a donor molecule, DTS(PTTh₂)₂ 21, based on an A/D/ A architecture comprising a dithieno(3,2-b; 2',3'-d)silole (DTS) core flanked by [1,2,5]thiadiazolo[3,4-c]pyridine (PT) acceptor units that was terminated with alkylated bithiophene (Th₂) donor groups (Fig. 9). Key to their synthetic approach was use of the asymmetric PT acceptor unit which enabled facile monofunctionalization owing to its unsymmetrical reactivity during the preparation of the intermediate A/D/A structure. BHJ solar cells fabricated using 21 and PC71BM acceptor as active layer materials were optimized using a small amount (0.25%) of 1,8diiodooctane (DIO) as a processing additive, resulting in the most efficient OPV devices based on small molecules prepared at the time. More recently, this research group has developed a similar donor molecule which replaces the pyridyl-based PT acceptor units with an asymmetric, fluorinated derivative.⁵⁴ Solar cells constructed using this small molecule analogue with PC71BM were able to achieve a remarkable PCE of 7.0%.

Although considerable OPV research has focused on designing new materials with ideal photophysical properties, the morphology of the active layer in BHJ solar cells is an equally important constraint.55 Materials that are purposeengineered to influence and control the assembly of donor and acceptor components are promising candidates for improving the performance of organic solar cells. For example, Nuckolls and coworkers^{57,58} designed a novel donor molecule, dibenzotetrathienocoronene (6-DBTTC, 22), based on the contorted hexabenzocoronene motif initially developed in 1958⁵⁶ which self-assembles into hole-transporting, columnar nanostructures upon thermal annealing (Fig. 10). Solar cells were prepared by spin casting 22 onto the electrode surface followed by annealing at 150 $^\circ\text{C}$ to afford a supramolecular, three-dimensional network of cables. The reticulated superstructure was subsequently filled with C_{60} via thermal evaporation to complete the active layer. A PCE of 1.9% was reported for the devices which were approximately three times higher than that observed for solar cells without nanostructured active layers. Even more remarkable is that a PCE approaching 2% could be achieved with a material that absorbs visible light relatively poorly (the bandgap of 22 is 2.8 eV). The authors note that solar cell performance is expected to improve significantly with a donor analogue that has greater absorption overlap with the solar spectrum.

CONCLUSIONS

The emergent demand for higher performance semiconductors has led to a resurgence of many organic materials developed in the past, in some cases first produced from natural sources thousands of years ago. Synthetic chemists have exploited the outstanding properties and synthetic availability of these pigments and transformed them into new families of π -conjugated building blocks for the construction of (macro)molecules with remarkable properties well-suited for organic electronic devices. The availability of diverse highperformance building blocks has allowed a new paradigm to take form in which these structural pieces are assembled into sophisticated and meticulously designed molecular structures with precise properties and functions. Almost certainly, the voluminous organic dye and pigment literature will continue to offer new building blocks and provide synthetic chemists with inspiration for cutting-edge materials capable of advancing OPV and OFET technology. If history holds true, the newest structure just might be found within the pages of an old article gathering dust.

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