This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

This article can be cited before page numbers have been issued, to do this please use: K. Nagarajan, A. R. Mallia, K. Muraleedharan and M. Hariharan, Chem. Sci., 2016, DOI: 10.1039/C6SC05126J.
Enhanced Intersystem Crossing in Core-Twisted Aromatics

Kalaivanan Nagarajan, Ajith R. Mallia, Keerthi Muraleedharan and Mahesh Hariharan*

We describe the design, bottom-up synthesis and X-ray single crystal structure of systematically twisted aromatics 1c and 2d for efficient intersystem crossing. Steric congestion at the cove region creates nonplanar geometry that induces significant yield of triplet excited state in the electron poor core-twisted aromatics 1c and 2d. A systematic increase in the number of twisted regions in 1c and 2d exhibits a concomitant enhancement in the rate and yield of intersystem crossing, as monitored using femtosecond and nanosecond transient absorption spectroscopy. Time-resolved absorption spectroscopic measurements display enhanced triplet quantum yield \((\Phi_3 = 10\pm1\% \text{ for } 1c, \text{and } \Phi_3 = 30\pm2\% \text{ for } 2d)\) in twisted aromatics when compared to negligible \(\Phi_3\) (<1\%) in the planar analog 3c. Twist-induced spin-orbit coupling via activated out-of-plane \(\text{C-H/C=C}\) vibrations can facilitate the formation of triplet excited state in twisted aromatics 1c and 2d, in contrast to negligible intersystem crossing in planar analog 3c. The ease of synthesis, high solubility, access to triplet excited state and strong electron affinity make such imide functionalized core-twisted aromatics as a desirable material for organic electronics such as solar cell.

Scheme 1. Molecular structure of the twisted derivatives 1c and 2d along with the planar derivative 3c (arrows indicate the cove and bay region in the derivatives)

Twist/non-planarity in enhancing the SOC in graphenoid structures (Table S1, Electronic Supplementary Information (ESI†)). Systematic incorporation of twist in heavy atom free17 sp\(^2\) hybridized graphenoid structure18 (Scheme 1) to activate intersystem crossing has received less attention. Though the effect of non-planarity on SOC is established in organic molecules,19 the phenomenon could not be generalized due to the observation of quantitative fluorescence in highly twisted chromophores.20

Our on-going interest with core-twisted21 organic chromophores22 prompted us to study the role of twist in the triplet formation. Recent efforts from our group on bay substitution with multiple bromine atoms reveal the core-twisted geometry of perylenediimide which exhibit enhancement in triplet generation.23 Though core-twisting of perylenediimide through bay substitution is well established, the studies were not focused on the intersystem crossing...
properties of the materials.\textsuperscript{24} To isolate the influence of twist from heavy atom effect, it is imperative to impart heavy atom free twist in the chromophoric structure. Bottom-up approach to synthesize non-planar aromatics,\textsuperscript{25} that include hexabenzo[1,2-c:4,5-c']coronene,\textsuperscript{26} hexabenzo[1,2-c:4,5-c']coronene,\textsuperscript{27} dibenzotetrathienocoronene,\textsuperscript{28} octabenzo[1,2-c:4,5-c']coronene,\textsuperscript{29} dimeric\textsuperscript{30} and core-twisted perylenediimides,\textsuperscript{31} is still an emerging area for diverse opto-electronic applications. Hydrogen-hydrogen repulsion induced steric congestion at the cove region of extended perylenediimide chromophore offered core-twisted aromatics \textit{a) and b) with FeCl}_{3} in dry DCM/CH\textsubscript{3}NO\textsubscript{2} solution under nitrogen atmosphere. Between 0-30 °C, cyclized products from \textit{a) and b) were formed in low yield (<1%). At higher temperature (40 °C), desired products \textit{c) and d) were obtained in 50% and 40% yield respectively under continuous nitrogen flow (Figures S1-S4, ESI†). Intermediate 2c (5% yield) was also isolated during the reaction and characterized by spectroscopic methods. Model planar derivative 3c (Figure 1c) was synthesized via Suzuki coupling of two benzene units with 1,7-dibromo PDI (2a) followed by Scholl dehydrogenation reaction. Red fluorescent single crystals of \textit{c) and d) were obtained from chloroform and toluene solution respectively.

\section*{Results and Discussion}

\textbf{Synthesis and Characterisation}

Compounds \textit{a) and b) were synthesized by Suzuki coupling of one and two phenanthrene units respectively with perylenediimide (PDI) following by the metal catalyzed Scholl dehydrogenation reaction (Figure 1a-b). Bromination and imidisation of 1 were performed by following the procedure reported elsewhere.\textsuperscript{21} To isolate the influence of twist from heavy atom effect, it is imperative to impart heavy atom free twist in the chromophoric structure. Bottom-up approach to synthesize non-planar aromatics,\textsuperscript{25} that include hexabenzo[1,2-c:4,5-c']coronene,\textsuperscript{26} hexabenzo[1,2-c:4,5-c']coronene,\textsuperscript{27} dibenzotetrathienocoronene,\textsuperscript{28} octabenzo[1,2-c:4,5-c']coronene,\textsuperscript{29} dimeric\textsuperscript{30} and core-twisted perylenediimides,\textsuperscript{31} is still an emerging area for diverse opto-electronic applications. Hydrogen-hydrogen repulsion induced steric congestion at the cove region of extended perylenediimide chromophore offered core-twisted aromatics \textit{a) and b) with FeCl}_{3} in dry DCM/CH\textsubscript{3}NO\textsubscript{2} solution under nitrogen atmosphere. Between 0-30 °C, cyclized products from \textit{a) and b) were formed in low yield (<1%). At higher temperature (40 °C), desired products \textit{c) and d) were obtained in 50% and 40% yield respectively under continuous nitrogen flow (Figures S1-S4, ESI†). Intermediate 2c (5% yield) was also isolated during the reaction and characterized by spectroscopic methods. Model planar derivative 3c (Figure 1c) was synthesized via Suzuki coupling of two benzene units with 1,7-dibromo PDI (2a) followed by Scholl dehydrogenation reaction. Red fluorescent single crystals of \textit{c) and d) were obtained from chloroform and toluene solution respectively.

\textbf{Crystal Structure Analysis}

Compound \textit{c} crystallized in tetragonal space group \textit{P-4_1} containing 4 molecules per unit cell (Table S2, ESI†). Repulsion between H1', H8' atoms of phenanthrene unit and H2, H11 atoms of PDI unit, at the cove region (Figure S5a, ESI†) twist the chromophore 1c. The twist angle was calculated from the angle between the perylenediimide and phenanthrene planes in the crystal structure (Figure S5b and d, ESI†). The twist angles at the two cove regions of the compound \textit{c} are found to be 44.3° and 40.7° (Figure 1d). Compound 2d possessing wagging\textsuperscript{1} conformation crystallizes in triclinic space group \textit{P-1}, having one molecule per unit cell (Table S2, ESI†). Repulsion between H1', H8' atoms of phenanthrene units and the pery region hydrogen atoms (H2, H5, H8 and H11) of PDI (Figure S5c, ESI†) at the 4 cove regions twist the chromophore 2d with a twist angle of 44.2° and 41.3° (Figure 1e). To evaluate the thermodynamic stability between the helical vs. wagging\textsuperscript{1} (Figure 2), conformation of the derivative 2d we conducted...
density functional theory (DFT) calculations at the B3LYP/6-311G+(d, p) level. From the DFT calculations, it is estimated that the waggling conformer of 2d is thermodynamically more stable than the helical conformer by 17.5 kcal mol$^{-1}$, which is in agreement with the waggling conformation obtained from the single crystal X-ray structure (Figure 2). Single crystal X-ray structure analysis of 1c and 2d revealed a core-twisted polycyclic skeleton having 9 and 13 aromatic rings respectively.

**Electrochemical Properties**

Cyclic voltammogram (0.1 M, nBu$_4$NPF$_6$ in DCM) exhibited reversible reduction peaks (Figure 3a) at -1.14 and -1.37 V for 1c; -1.22 and -1.46 V for 2d (Table S3, ESf†) with reference to Fc/Fc$^+$ electrode. The reduction potential of the derivatives 1c and 2d are more negative than those of the model derivative 3c (-1.00 and -1.24 V), indicating that the 1c and 2d derivatives are significantly weaker electron acceptors. Highest occupied molecular orbital (HOMO) distribute over the whole π system of the derivatives 1c, 2d and the model derivative 3c (Figure 5, ESf†). In contrast, lowest unoccupied molecular orbital (LUMO) spreads only at the coronenediimide core, due to the presence of electron withdrawing imide group.

**Photophysical Charaterisation**

By virtue of the twisted nature, derivatives 1c and 2d with large π-surface dissolve well in common organic solvents like chloroform, dichloromethane and toluene. UV-Vis absorption spectrum (Figure 3b) of 1c in toluene shows peaks centered at 475, 505 and 545 nm corresponding to π→π$^*$ (HOMO→LUMO) transition (Table S4, ESf†). Derivative 2d in toluene exhibits π→π$^*$ transition at i) 582 and 539 nm corresponding to S$_2$→S$_1$ (HOMO→LUMO); ii) 475, 445 and 416 nm due to S$_3$→S$_1$ (HOMO-1→LUMO); iii) 385 nm corresponding to S$_3$→S$_2$ (HOMO→LUMO+1), in agreement with the DFT calculations (Figure 3b). Model derivative 3c exhibits peak centered at 460 and 490 nm corresponding to π→π$^*$ (HOMO→LUMO) transition as reported earlier. Upon excitation at 480 nm, 1c shows vibronically resolved emission (Figure 3c) centered at 555, 597 and 652 nm with the fluorescence quantum yield (Φ$_f$) of 70%. Temperature dependent emission ($\lambda_{ex}$=480 nm) and excitation ($\lambda_{em}$=600 nm) spectra of 1b in toluene indicated the evolution of a new species having fluorescence emission features identical to that of 1c (Figure S7a-b, ESf†). Spectroscopic analysis confirms the photocyclization of 1b in toluene (ca. 1 μM) at higher temperature to yield 1c. When compared to 1c, derivative 2d exhibits red-shifted emission centered at 586, 635 and 696 nm with Φ$_f$ of 40%. Model derivative 3c show vibronically resolved emission centered at 510, 550 and 580 nm with Φ$_f$ of 85% (Table S4, Figure S8a, ESf†). Partial reduction in the Φ$_f$ of 1c and 2d when compared 3c could be attributed to the non-radiative decay pathways arising from nonplanar nature of the chromophores 1c and 2d. Upon excitation at 480 nm, derivative 1c and 2d in toluene exhibit fluorescence lifetime (Figure 3d) of 10 and 5.4 ns respectively. Model derivative 3c in toluene shows monoexponential fluorescence lifetime of 5.5 ns upon excitation with 480 nm (Figure S5b, ESf†).

**Nanosecond Transient Absorption Measurements**

Further insights into the excited state deactivation in core-twisted derivatives came from nanosecond and femtosecond transient absorption measurements. Upon excitation at 355 nm, 10 ns laser pulse, 1c in toluene (Figure 4a) exhibited the negative absorption peaks centered at 380, 470 and 510 nm corresponding to ground state depletion (S$_0$→S$_1$). Due to the stronger positive signal at 520-620 nm, ground state bleach at 520 to 570 nm is not seen in the nTA spectra as compared to the UV-Vis absorption spectra. Observed twin absorption centered at 400 and 580 nm with the single exponential decay lifetime of 3.7 μs (Figure 4b) is attributed to triplet excited state in 1c. Compound 2d in toluene (Figure S9a, ESf†) showed ground state depletion at 390, 480 and 590 nm, consistent with the UV-Vis absorption spectrum. Transient absorption corresponding to triplet excited state is observed at 340, 420, 560 and 610 nm with the lifetime of 19.6 μs (Table S4, Figure S9b, ESf†). The existence of triplet excited state in 1c and 2d were further confirmed by the quenching of the transient spectra by oxygen purging. In contrast, planar derivative 3c in toluene exhibited negligible transient absorption upon excitation at 355 nm. Triplet quantum yield (Φ$_f$) of 1c and 2d...
were calculated to be 10±1% and 30±2% (Table S4, ESI†) respectively employing triplet-triplet energy transfer method.21 Significant enhancement in the Φ of 1c and 2d when compared to the model derivative 3c is attributed to the twist induced SOC as reported earlier.19 However, ISC was reported by Flamigni and coworkers in unsymmetrically substituted planar perylene derivatives which could be attributed to the nπ* to ππ* transition arising from the bay imidisation.36 Attempts to record the phosphorescence in the core-twisted derivatives 1c and 2d was not successful in DCM-EtOH glass at low temperature (77K). However the derivatives 1c and 2d exhibit phosphorescence in DCM-EtOH-CH3I (1:1:0.1) glass at low temperature (77K, Figure S10, ESI†).

Femtosecond Transient Absorption Measurements

To unravel the kinetics of intersystem crossing, core-twisted derivatives 1c and 2d in toluene were excited with 110 fs, 300 nm laser pulse. Femtosecond transient absorption (FTA) spectra of 1c and 2d showed a sharp negative absorption at 600 nm, corresponding to the second harmonic of the pump laser (2λex = 600 nm). Photoexcitation of 1c at 300 nm displayed (Figure 4c) negative absorption at 505 and 545 nm along with the positive absorption peaks centered at 510, 550, 630, 680 and 720 nm. Negative absorption observed at 505 and 545 nm could be ascribed to ground state depletion of 1c and 2d in toluene (Figure S9c, ESI†) showed ground state depletion at 475, 532 and 585 nm, consistent with the ground state absorption spectrum. SVD followed by global analyses of the positive absorption bands centered at 455, 516, 552 and 610-800 nm consist of three principal components (Figure S12, ESI†). Negative absorption centered at 600 nm, with the lifetime of 5.1 ns is attributed to stimulated emission. The right singular vector at 720 nm decays with a lifetime of 6.5 ps (kISC = 1.54x10¹¹ s⁻¹) that corresponds to S₁→S₅ transition (Figure S9d, ESI†). During the decay centered at 720 nm, concomitant appearance of a new band at 630 nm is observed (Figure S9c, ESI†). Emerging band at 630 nm with a rise time (τISC) of 25 ps (kISC = 4x10¹⁰ s⁻¹) is attributed to T₁→T₉ transition in the derivative 2d. According to the rates of internal conversion (kIC) and intersystem crossing (kISC), the efficiency of ISC (φISC = kISC/kIC) is calculated to be 7.1% and 26% for 1c and 2d respectively which is in agreement with the Φs calculated from the triplet-triplet energy transfer method. Quantum chemical calculations (Figure S13, ESI†) indicate that out of plane C=C and C-H vibrations (νop) can allow efficient ISC from a nπ* type singlet to ππ* type triplet driven by Herzberg–Teller vibronic coupling in the core-twisted derivatives 1c and 2d.37

Conclusions

In conclusion, we report the design and synthesis of solution processable electron deficient core-twisted aromatics 1c and 2d. Femtosecond and nanosecond transient absorption measurements revealed “twist-only” induced ultrafast ISC in the non-planar derivatives 1c and 2d. Enhanced out of plane C=C and C-H vibrations facilitate efficient ISC with Φ of 10±1% and 30±2% in the derivatives 1c and 2d respectively, driven by Herzberg–Teller vibronic coupling. Higher kISC of 4x10¹⁰ s⁻¹ for doubly twisted 2d when compared to kISC of 1x10⁹ s⁻¹ for singly twisted 1c clearly establishes the role of non-planarity in facilitating ISC in the reported derivatives 1c and 2d. Ease of solution processability and activated triplet excited state in the twisted aromatics 1c and 2d are beneficial for solar energy conversion by virtue of their long-lived triplet excited state. Current efforts in our laboratory are directed towards developing twisted chromophores for high performance optoelectronic devices.

Experimental Section

Spectral Measurements: Absorption spectra were recorded in Shimadzu UV-3600 UV-VIS-NIR while emission (fluorescence/phosphorescence) and excitation spectra were performed in Horiba Jobin Yvon Fluorolog spectrometer. All spectroscopic experiments were performed by using standard quartz cuvettes of path length 1 cm for solution in dried and distilled solvents. The solution state fluorescence quantum yields were determined by using optically matched solutions. Fluorescein dissolved in ethanol (ΦF = 0.79)38 was used as the standard. Φs of the samples were calculated as follows,

Figure 4. a) nTA spectra and b) corresponding decay profile of 1c upon excitation with 355 nm in toluene; c) FTA spectra and d) corresponding decay profile of 1c upon excitation with 300 nm in toluene.
Nanosecond Transient Absorption Measurements: Laser flash photolysis experiments of the nitrogen purged solutions were carried out in an Applied Photophysics Model LKS-60 laser kinetic spectrometer using the second and third harmonic (355 nm and 532 nm, pulse duration ≈10 ns) of a Quanta Ray INDI-40-10 series pulsed Nd:YAG laser. Triplet states of the excited aromatics 1c and 2d in toluene were confirmed using the measurement of oxygen purged solutions through nanosecond flash photolysis studies. Triplet quantum yields \( \Phi_{\text{t}} \) obtained upon direct photoexcitation (355 nm) were determined by using [Ru(bpy)]Cl\(_2\) in methanol as standard (\( \Phi_{\text{t}} = 1 \)), with nonsaturating laser intensities. Equal volume of 0.2 mM solution of \( \beta \)-carotene was added to optically matched solutions of reference and the sample. The equation for the triplet quantum yield is given by,

\[
\Phi_{\text{t}} = \Phi_{\text{t}}^{\text{ref}} \times \frac{\Delta A^\text{t}}{\Delta A^\text{ref}} \times \frac{k_{\text{obs}}}{k_{\text{obs}}^{\text{t}}} \times \frac{k_{\text{obs}}^{\text{ref}} - k_{\text{t}}^{\text{ref}}}{k_{\text{obs}}^{\text{t}} - k_{\text{t}}^{\text{t}}} \tag{2}
\]

where, \( \Phi_{\text{t}}^{\text{t}} \) and \( \Phi_{\text{t}}^{\text{ref}} \) denote the triplet quantum yield of the sample and reference respectively; \( \Delta A^\text{t} \) and \( \Delta A^\text{ref} \) are transient absorption intensity of \( \beta \)-carotene in sample and reference respectively; \( k_{\text{obs}}^{\text{t}} \) and \( k_{\text{obs}}^{\text{ref}} \) are decay rate of sample transient species before and after the addition of \( \beta \)-carotene. \( k_{\text{obs}}^{\text{ref}} \) and \( k_{\text{obs}}^{\text{t}} \) are decay rate of reference transient species before and after the addition of \( \beta \)-carotene.

Femtosecond Transient Absorption Measurements: Spectra-Physics Tsunami Oscillator (80 MHz, 800 nm) was used as seed for a Spectra-Physics Spitfire Regenerative amplifier (1 KHz, 4 mJ). A fraction of the amplified output was used to generate 300 nm pump pulse. Residual 800 nm pulse was sent through a delay line inside an Exciplex pump-probe spectrometer from CDP Systems. A rotating CaF\(_2\) plate (2 mm thickness) was used to generate continuum of white light from the delayed 800 nm pulses. The continuum of white light was split into two and the streams were used as probe and reference pulses. Transient absorption spectra were recorded using a dual diode array detector with a 200 nm detection window. Sample solutions were prepared in a rotating sample cell with 400 \( \mu \)m path length. IRF was determined by solvent (10% Benzene in Methanol) two photon absorption and was found to be approximately 130 fs at about 530 nm. Energy per pulse incident on the sample is attenuated employing 80% neutral density filter when required. Toluene solution of the derivatives 1c, 2d were pumped with 300 nm, 200 nJ, \( \sim \)110 fs laser pulses and probed by the white light. Singular value decomposition (SVD) of \( \Delta A \) versus time and wavelength based three-dimensional map of the derivatives 1c and 2d obtained from fTA measurements. For SVD, the fTA spectra of 1c and 2d were constructed into a matrix in the Origin graphics software program (Version 8.5; MicroCal, Inc., Northampton, MA). Global analyses of the fTA spectra of the derivatives 1c and 2d were carried out using Glotaran (version 1.2). \(^{40}\)

Efficiency of intersystem crossing (\( \Phi_{\text{ISC}} \)) could be estimated from the rates of internal conversion (\( k_{\text{IC}} \)) and intersystem crossing (\( k_{\text{ISC}} \)) as follows, \(^{41}\)

\[
\Phi_{\text{ISC}} = \frac{1}{\tau_{\text{ISC}}} \times \frac{1}{\tau_{\text{IC}}} \tag{3}
\]

where, \( \tau_{\text{ISC}} \) = rate of intersystem crossing and \( \tau_{\text{IC}} \) = rate of internal conversion; extracted from the fTA spectra analysis.

X-ray Crystallography: High-quality specimens of appropriate dimensions were selected for the X-ray diffraction experiments. Crystallographic data collected are presented in the supplementary information. Single crystals were mounted using oil (Infinium V8512) on a glass fibre. All measurements were made on a CCD area detector with graphite monochromated Mo K\( \alpha \) radiation. The data was collected using Bruker APEX2 detector and processed using APEX2 from Bruker. All structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions, but not refined. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. The full validation of CIFs and structure factors of 1c and 2d were performed using the CheckCIF utility and found to be free of major alert level. 3D structure visualization and the exploration of the crystal packing of the derivatives were carried out using Mercury 3.1.

Computational Methods: Ground-state optimised structure and harmonic oscillator frequencies were computed using density functional theory (DFT) at the Beake’s three parameter functional in combination with the Lee-Yang-Parr correlation functional (B3LYP) and 6-311++G(d,p) basis set. Vertical excitation energies and oscillator strengths were calculated employing time dependent DFT (TD-DFT) at the B3LYP/6-311++G(d,p) level of theory. All computations were performed with the Gaussian 09 program suite. \(^{44}\)

Acknowledgements

Authors thank Nanobiotechnology Task Force, DBT, Govt. of India for the support, BT/PR5761/NNT/106/599/2012; A. P. Andrews for X-ray analysis; K. Nagaraj for femtosecond transient absorption measurements. K. N. acknowledges University Grants Commission (UGC), India; A. R. M. thanks Council of Scientific & Industrial Research (CSIR) for fellowship and K. M. thanks INSPIRE for fellowship.

Notes and references

1. M. Ball, Y. Zhong, Y. Wu, C. Schenck, F. Ng, M. Steigerwald, S. Xiao and C. Nuckolls, Acc. Chem. Res., 2015, 48, 267-276.
2. J. R. Sanchez-Valencia, T. Dienel, O. Groning, I. Shorubalko, A. Mueller, M. Jansen, K. Amsharov, P. Ruffieux and R. Baumeister, J. Lee, B. Yeom, J. H. Bahng, J. Lee, A. Violi and N. A. Kotov, Angew. Chem. Int. Ed., 2009, 48, 7668-7672.
3. Z. Liu, A. C. Fan, K. Rakrha, S. Sherlock, A. Goodwin, X. Chen, Q. Yang, D. W. Felscher and H. Dai, Acc. Chem. Res., 2016, 512, 61-64.
4. N. Suzuki, Y. Wang, P. Elvati, Z.-B. Qu, K. Kim, S. Jiang, E. Baumeister, J. Lee, B. Yeom, J. H. Bahng, J. Lee, A. Violi and N. A. Kotov, ACS Nano, 2016, 10, 1744-1755.

This journal is © The Royal Society of Chemistry 20xx J. Name., 2013, 00, 1-3 | 5
5. A. Modl, N. Koratkar, E. Lass, B. Wei and P. M. Ajayan, Nature, 2003, 424, 171-174.
6. (a) J. V. Urbanova, F. Karlicky, A. Matej, F. Sembera, Z. Janousek, J. A. Perman, V. Ranc, K. Cepe, J. Michl, M. Otyepka and R. Zboril, Nanoscale, 2016, 8, 12134-12142; (b) A. K. Geim and K. S. Novoselov, Nat. Mater., 2007, 6, 183-191.
7. M. L. Mueller, X. Yan, J. A. McGuire and L.-S. Li, Nano Lett., 2010, 10, 2679-2682.
8. J. Balakrishnan, G. Kok Wai Koon, M. Jaiswal, A. H. Castro Neto and B. Ozyilmaz, Nat. Phys., 2013, 9, 284-287.
9. S. Imr, T. Frank, S. Putz, M. Gmitra, D. Kochan and J. Fabian, Phys. Rev. B, 2015, 91, 115141.
10. A. Vars, J. Y. Tan, T. Tsichrintznatap, J. Balakrishnan, G. K. Koon, Y. Yeo, J. Lahiri, A. Carvalho, A. S. Rodin, E. C. O'Farrell, G. Eda, A. H. Castro Neto and B. Ozyilmaz, Nat. Commun., 2014, 5, 1-6.
11. D. Marchenko, A. Varkyhalov, M. R. Scholz, G. Bihlmayer, E. I. Rashba, A. Rybkin, A. M. Shikin and O. Rader, Nat. Commun., 2012, 3, 1232.
12. M. Kralj, Nat. Phys., 2015, 11, 11-12.
13. C. Weeks, J. H. Jalicea, M. Franze and R. Wu, Phy. Rev. X, 2011, 1, 021001-021015.
14. J. W. Arbogast and C. S. Foote, J. Am. Chem. Soc., 1991, 113, 8886-8899.
15. T. Vosch, J. Hofkens, M. Cotlet, F. Kohn, H. Fujiwara, R. Groneheid, K. Van Der Biest, T. Weil, A. Herrmann, K. Müllen, S. Mukamel, M. Van der Auweraer and F. C. De Schryver, Angew. Chem. Int. Ed., 2001, 40, 4643-4648.
16. (a) J. F. Lewis and X. Zuo, J. Am. Chem. Soc., 2003, 125, 8806-8813; (b) D. Huertas-Hernando, F. Guinea and A. Brataas, Phy. Rev. B, 2006, 74, 155426.
17. O. Bolton, K. Lee, H.-J. Kim, Y. Lin and J. Kim, Nat. Chem., 2011, 3, 205-210.
18. Y. Li, Z. Jia, S. Xiao, H. Liu and Y. Li, Nat. Commun., 2016, 7.
19. K. Schmidt, S. Brovell, V. Coropceanu, D. Beljonne, J. Cornil, C. Bazzini, T. Caronna, R. Tubino, F. Meirand, Z. Shuai and J.-L. Brédas, J. Phys. Chem. A, 2007, 111, 10490-10499.
20. (a) Y. Zagranjarski, L. Chen, D. Jänisch, T. Gessner, C. Li and K. Müllen, Org. Lett., 2014, 16, 2814-2817; (b) J. F. Würthner, in Pure Appl. Chem., 2006, vol. 78, p. 2341; (c) J. Hofkens, T. Vosch, M. Maus, F. Kohn, M. Cotlet, T. Weil, A. Herrmann, K. Müllen and F. C. De Schryver, Chem. Phys. Lett., 2001, 333, 255-263; (d) J. Chen, U. Baumeister, C. Scharschke and F. Würthner, Chem. Eur. J., 2007, 13, 450-465.
21. K. Nagarajan, A. R. Mallia, V. S. Reddy and M. Hariharan, J. Phys. Chem. C, 2016, 120, 8443-8450.
22. (a) A. R. Mallia, P. S. Salimi and M. Hariharan, J. Am. Chem. Soc., 2015, 137, 15604-15607; (b) T. Cheryia, A. R. Mallia and M. Hariharan, Energy Environ. Sci., 2014, 7, 1661-1669.
23. (a) J. Jimenez, M.-J. Lin, C. Burschka, J. Becker, V. Settels, B. Engels and F. Würthner, Chem. Sci., 2014, 5, 608-619; (b) Y. Cai, L. Hau, X. Sun, D. Wei, M. Tang and Y. Sun, Adv. Energy Mater., 2015, 5, 1500032-1500036; (c) P. Osswald and F. Würthner, J. Am. Chem. Soc., 2007, 129, 14319-14326.
Chemical Science

Core-twisted aromatics exhibit enhanced intersystem crossing when compared to the planar analog upon photoexcitation.

J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Wallingford, CT, USA, 2009.

35. C. Lütke Eversloh, C. Li and K. Müllen, Org. Lett., 2011, 13, 4148-4150.

36. (a)L. Flamigni, A. Zanelli, H. Langhals and B. Böck, J. Phys. Chem. A, 2012, 116, 1503-1509; (b)B. Ventura, H. Langhals, B. Bock and L. Flamigni, Chem. Commun., 2012, 48, 4226-4228.

37. B. R. Henry and W. Siebrand, J. Chem. Phys., 1971, 54, 1072-1085.

38. D. F. Eaton, Pure Appl. Chem., 1988, 60, 1107-1114.

39. W. E. Ford and P. V. Kamat, J. Phys. Chem., 1987, 91, 6373-6380.

40. J. J. Snellenburg, S. P. Laptenok, R. Seger, K. M. Mullen and I. H. van Stokkum, J. Stat. Softw., 2012, 49, 1-22.

41. Y. Wu, Y. Zhen, Y. Ma, R. Zheng, Z. Wang and H. Fu, J. Phys. Chem. Lett., 2010, 1, 2499-2502.