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Exceptionally Strong Electronic Coupling in Crystalline Perylene Diimides via Tuning

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Supporting Information

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Perylene diimides (PDIs) are among the best n-type organic semiconductors in part owning to their large driving force to form π-stacks.[1] The short intrastack separation of PDI cores allows a significant coupling of frontier orbitals, so orbital energy levels split forming bands. A stronger HOMO/LUMO coupling produces a broader valence/conduction band, which leads to an increased λ_{max} in an electronic absorption spectrum due to the reduced band gap.[2] As the HOMO and LUMO levels of individual core-unsubstituted PDI (CUPDI) molecules have little dependence on the imide substituent (R),[1] the λ_{max} is an indicator of the overall HOMO/LUMO coupling magnitude in a CUPDI. A longer λ_{max} is generally associated with a stronger HOMO/LUMO coupling and a better capability to absorb sunlight.[3] Thus there is a strong motivation to develop solid CUPDIs with the longest possible λ_{max} for photovoltaic applications.[4] The broad valence/conduction bands implied by a very long λ_{max} are correlated with improved charge transport,[5] which makes such PDIs even more appealing for photovoltaics and for organic (opto)electronic applications in general.

Despite the promising value, CUPDIs with a very long λ_{max} have not been systematically pursued experimentally, to the best of our knowledge. In contrast, the corresponding computational research has advanced considerably.[2,5,6] In a solid π-stacked PDI, the interaction inside a one-dimensional π-stack accounts for most of the intermolecular electronic coupling.[5a] As the perylene interplanar spacing is always around 3.5 Å in a parallel piled stack as found in most crystalline CUPDIs, the intrastack offset values along the long (x) and short (y) axes of the PDI ring as illustrated in Figure 1a become the key parameters determining the electronic coupling.[2] When molecules stack the shift of absorption spectra is generally mainly determined by exciton interactions which do not require molecular orbital overlap. However, just as for orbital overlap the size and even sign of this exciton interaction will be a very sensitive function of the x and y displacements.[7] Recently the intrastack binding energy and intermolecular coupling of frontier orbitals, as a function of x and y offset values, have been computed extensively.[5,6a] The set of x and y offset values for a very long λ_{max} has been suggested.[5b,6a] However, to design a PDI molecule that can materialize a planned packing geometry remains a challenge, as to date the desired R-packing relationship cannot be known before the crystal structure is solved.[5a] Although a number of CUPDIs with a strong intermolecular HOMO/LUMO coupling exhibiting the λ_{max} up to 678 nm have been reported, most of them were discovered serendipitously.[8] Slightly modifying the R of an existing long-λ_{max} CUPDI as an approach to improve the λ_{max} is likely to fail, as it is known that the λ_{max} is highly sensitive to even a slight change of R,[2,5a,8a] which can be ascribed to the relatively flat binding energy surface of parallel stacked PDI units.[5b,6a] With a fairly flat PDI binding energy surface, the packing is practically dictated by the R and its subtle adjustment may lead to a dramatic change in x and/or y offset values to avoid unfavorable interactions or to maximize favorable interactions. On the other hand, if only a small and incremental change of x and/or y offset values occurs upon an incremental adjustment of the R, very long λ_{max} values may be achieved by a tuning approach. To make the tuning productive, the R should provide additional intermolecular interactions that are robust enough to suppress dramatic structural changes while allowing a fine-tuning of x and/or y offset values, in addition to being able to induce a strong intermolecular electronic coupling between PDI cores.

Here we report the discovery of 4-n-alkoxy-4-oxobutyl groups as the first such substituents. By gradually altering the n-alkyl chain, the λ_{max} of solid **G*n*** has been systematically tuned up to 695 nm. The unprecedentedly long λ_{max} implies an exceptionally strong intermolecular HOMO/LUMO coupling.

The general structure of **G*n*** is shown in Figure 1a. Their dilute (2.65×10^{-5} mol/L) chloroform solutions exhibit the same UV spectrum, just as other CUPDIs.[1] The spectrum (Supporting Information Figure S1) features a series of absorption peaks at 527, 490, and 458 nm. Upon the addition of methanol, a dramatically red-shifted peak ($\lambda_{max} \geq 640$ nm) appeared, as shown in Figure 1b, due to the formation of PDI crystals. The λ_{max} values are listed in Table 1 along with those from solution-cast solid **G*n*** films whose spectra are presented in Supporting Information Figure S2. The picture of a **G8** chloroform solution (2 mg/mL) and a film cast from it are shown in Figure 1c. All these compounds exhibit dramatically red-shifted (>110 nm) λ_{max} values in the solid state with respect to that of the unassociated state in dilute chloroform solutions, which indicates that (4-n-alkyoxy)-4-oxobutyl groups can indeed consistently induce a large intermolecular frontier orbital overlap. While such a structure-directing

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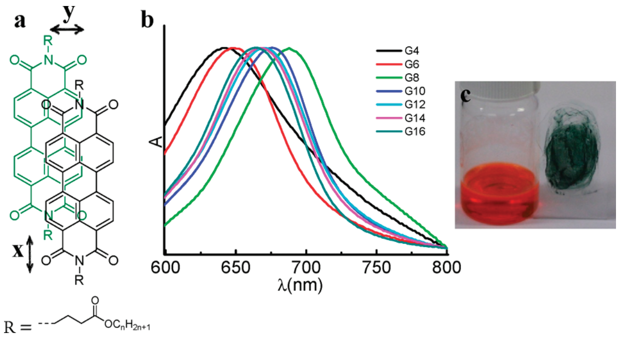

Figure 1. (a) Diagram of two stacked **G*n*** molecules showing displacements along the long (x) and short (y) axes of the perylene ring; the y offset value was exaggerated for clarity; $n = 4, 6, 8, 10, 12, 14, 16$. (b) UV spectra (normalized at the λ_{max} values) of **G*n*** in 2/1 (v/v) methanol/chloroform binary solvent. (c) Picture of a **G8** chloroform solution (2 mg mL^{-1}) and a solid film cast from it.

Table 1. λ_{max} Values in Figure 1b, λ_{max} Values of G*n* Films, and $\nu_{C=O}$ Values of Ester Groups in Solid G*n*

n	λ_{max} (nm) in Figure 1b	λ_{max} (nm) of solid films	$\nu_{C=O}$ (cm^{-1})
4	647	642	1738.1
6	680	654	1739.0
8	695	692	1742.4
10	687	683	1742.9
12	676	676	1743.8
14	670	670	1745.6
16	667	665	1746.7

effect is robust since all **G*n*** solids are of strong electronic coupling despite the large variation of n, it still permits small-scale changes in the local PDI packing mode as reflected by the n-dependent λ_{max} values. It is intriguing that the variation is systematic: The λ_{max} first increases with n until the longest λ_{max} at $n = 8$. Afterward, further increase of n results in a slight but continuous decrease of the λ_{max} value.

The robust structure-directing effect of (4-*n*-alkyoxy)-4-oxobutyl groups is also supported by X-ray diffraction results. The powder patterns (Supporting Information Figure S3) illustrate the crystalline order of these compounds. The strongest diffraction in the small-angle region is attributed to the layered structure arising from the microphase separation between the PDI core and *R*. Its *d*-spacing represents the periodicity of the layered structure and is plotted versus n in Figure 2. The nearly linear relationship suggests that the local packing schemes of PDI cores are very similar among all homologues, in other words, robust against the variation of n.

SEM images shown in Supporting Information Figure S4 illustrate the morphology of the **G*n*** aggregates grown from 2/1 (v/v) methanol/chloroform binary solvent. Just like many CUPDIs with unbranched *N*-substituents,[9] micro/nanobelts are the major form of aggregation. This is especially true for **G8**, **G10**, **G12**, **G14**, and **G16**, as both flat-on and side-on belts can be observed. **G4**, **G6**, **G8**, **G10**, and **G12** belts are typically longer than 10 μm. The exact length of **G14** and **G16** belts is more difficult to determine because they bend/twist more frequently than other homologues. However, the length of **G14** and **G16** belts is at least several micrometers and much greater than the corresponding width.

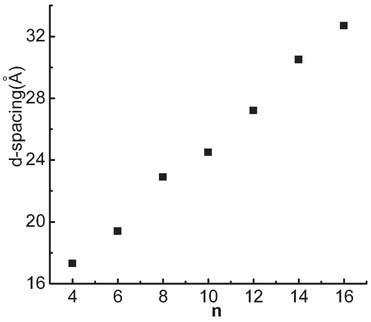

Figure 2. Periodicity values of the layered structure in solid **G*n***.

The width of **G*n*** belts is n-dependent. **G4**, **G6**, and **G8** belts feature a width about 1−2 μm. In contrast, the average widths of **G10**, **G12**, **G14**, and **G16** are 0.8 μm, 0.6 μm, 0.25 μm, and 0.15 μm, respectively. Due to the dramatically red-shifted λ_{max} values with respect to that of the monomeric state in a dilute solution, these aggregates can be considered as J-aggregates. Although we cannot completely exclude the possibility that the size of a **G*n*** aggregate may affect its λ_{max}, its contribution to the $\lambda_{max}-n$ correlation is likely to be small. This is because the electronic interaction inside a PDI π-stack accounts for the most of intermolecular electronic interactions[5a] and the π-stacking direction of **G*n*** molecules is expected to be along the belt long axis, similar to other CUPDI micro/nanobelts[9] or wires.[10] With at least thousands of PDI units well correlated along the belt long axis/π-stacking direction, we do not expect that a size difference can lead to a significantly different electronic coupling.

Therefore, the observed $\lambda_{max}-n$ correlation indicates that structural tuning is operative. We believe that the robust structure directing effect of (4-*n*-alkyoxy)-4-oxobutyl groups is one of the enabling factors. It is well-known that ester groups can engage in a relatively strong dipole−dipole attractive interaction[11] that exhibits a weaker distance dependence (r^{-3}) than attractive dispersion forces (r^{-6}),[6a] which makes it more tolerable to small-scale structure changes. Therefore it is speculated that the ester group is making an important contribution in the robustness of (4-*n*-alkyoxy)-4-oxobutyl groups' structure directing effect. The ester dipole−dipole interaction was probed by FTIR as it manifests as a red-shifted C═O stretching frequency ($\nu_{C=O}$).[11] Supporting Information Figure S5 presents a set of spectra showing the ester $\nu_{C=O}$ region of **G*n***. The peak positions range from 1738.1 to 1746.7 cm^{-1}, as given in Table 1. The $\nu_{C=O}$ value of truly noninteracting ester groups in **G*n*** is expected to be similar to or slightly higher than that of butyl acetate in the vapor phase, which is at about 1765 cm^{-1},[11a] as the potentially influencing imide group is electron withdrawing. The significantly lowered (by 18−27 cm^{-1}) $\nu_{C=O}$ values imply that ester groups in solid **G*n*** are indeed engaged in an attractive dipole−dipole interaction. Interestingly, the ester $\nu_{C=O}$ continuously increases when n increases. As the electronic effect of *n*-alkyl groups in **G*n*** are essentially the same, such a $\nu_{C=O}-n$ correlation reveals that ester groups in solid **G*n*** are experiencing a weaker dipole−dipole interaction with a larger n.[11] A (4-*n*-alkyoxy)-4-oxobutyl group consists of two subunits: the *n*-alkyl group as the adjustable component and the remaining part containing the ester group. Each subunit has its own most preferred local packing mode. Ester groups favor a strong dipole−dipole attractive force,[12] while *n*-alkyl groups prefer to pack tightly in the all-anti conformation as found in a *n*-alkane crystal.[13] The all-anti conformation of *n*-alkyl chains in

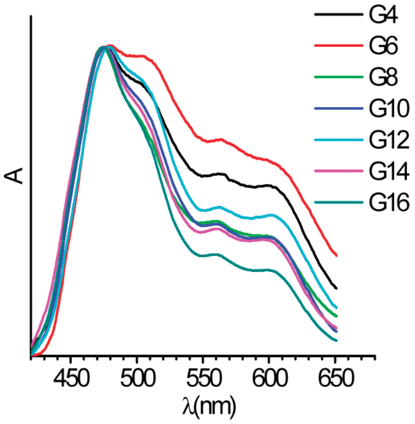

Figure 3. UV spectra of solid **G*n*** in the high temperature phase (spectra were taken at 160 °C for **G8**−**G16**, 170 °C for **G6** and 180 °C for **G4**).

G*n* is supported by FTIR results as shown in Supporting Information. We propose that the optimum packing of each subunit requires its own set of *x* and *y* offset values from π-stacked PDI cores when forming a **G*n*** crystal and two sets of offset values do not coincide, so two subunits have to compete for their energetic optimization. When a compromise is made, the final set of *x* and *y* offset values reflects the relative strengths of the two competing parties. Since a larger *n* enhances the *n*-alkyl group in the competition, the packing of PDI cores in **G4** features the strongest ester dipole interaction as it faces the weakest competition from *n*-alkyl chains. From there every stepwise increase of *n* changes the *x* and *y* offset values of PDI cores slightly in the direction that *n*-alkyl chains favor. The packing of PDI cores in **G16** is under the strongest influence from the *n*-alkyl chains so that it features the weakest ester dipole interaction, as evidenced by the highest $\nu_{C=O}$. From **G4** to **G16**, the ester dipole−dipole attractive interaction is always maintained thanks to its strength and weaker distance dependence, though its magnitude is slightly reduced with every stepwise increase of *n* due to the increased competition from the *n*-alkyl group. It plays a critical role of suppressing a dramatic change but allowing a fine adjustment on the PDI core local packing scheme upon a stepwise increase of *n*. Judged by the frequency shift, the strength of ester dipole interaction in **G*n*** is modest when compared with the strong ones in lactones with a bathochromic shift greater than 60 cm^{-1}.[11b] Such a modest interaction is advantageous for the tuning to be productive. If it is too weak, abrupt packing changes may occur. If it is too strong, *n*-alkyl chains will have difficulty to compete and generate a sizable λ_{max} variation. This may explain why in a series of long-λ_{max} CUPDIs induced by hydrogen bonding the significant variation of alkyl chains did not produce a considerable λ_{max} change.[8d]

One prediction that can be made on the basis of the proposed competition-based tuning is that the observed tuning effect will diminish or even vanish if the *n*-alkyl chains become disordered, because in this case the intermolecular π-orbital overlap will be mainly governed by the PDI π-stacking and the ester dipole−dipole. This is exactly what was observed in the high temperature phase of **G*n***s. All **G*n***s exhibit this phase between the room temperature crystalline phase and the isotropic melt. FTIR and X-ray diffraction results indicated that in this phase the PDI cores are π-stacked and the *n*-alkyl chains are in the liquid-like disordered conformation, as given in Supporting Information. The UV spectra shown in Figure 3 demonstrated that all **G*n***s share the essentially the same λ_{max} value in this phase. Moreover, as shown in Supporting Information Figure S8, the ester $\nu_{C=O}$ of **G*n***s are all at about 1740 and 1722 cm^{-1}, despite the large variation of *n*. The appearance of two ester $\nu_{C=O}$ bands implies that ester groups are in two different local environments, which has been reproduced by our molecular simulation as presented in Supporting Information. Without the competition from ordered *n*-alkyl chains, on average the ester groups are enjoying appreciably stronger dipole−dipole interaction, as indicated by the significantly lower average $\nu_{C=O}$ value. This provides further support to our proposed competition-based tuning mechanism.

As the result of this tuning process, **G6**, **G8**, and **G10** exhibit a λ_{max} greater than the previously reported longest λ_{max}.[8a] **G8** shows a λ_{max} of 695 nm that matches nearly perfectly with the solar flux peak wavelength (~700 nm). This, in combination with the expected high charge carrier mobility associated with the exceptionally strong electronic coupling, makes **G8** an extremely appealing photovoltaic material.

In conclusion, we have discovered the first *R*s that can robustly lead to solid CUPDIs with a strong and tunable electronic coupling. The tuning effect was attributed to the competition between two subunits in a *R*. By varying the length of *n*-alkyl chains, solid CUPDIs with an extraordinarily long λ_{max} were successfully generated. This tuning approach enables us to control the electronic coupling in solid CUPDIs at a new level. This new crystal engineering approach may also be applied to other π-stacked organic semiconductors and produce an exciting array of materials with engineered (opto)electronic properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures, synthesis of compounds, and details on the characterizations as well as simulation of solid **G*n***s. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Würthner, F. *Chem. Commun.* **2004**, 1564–1579 and the references therein.

(2) Kazmaier, P. M.; Hoffmann, R. *J. Am. Chem. Soc.* **1994**, *116*, 9684–9691.

(3) Case, M. A.; Owusu, Y. A.; Chapman, H.; Dargan, T.; Ruscher, P. *Renewable Energy* **2008**, *33*, 2645–2652.

(4) (a) Pandey, A. K.; Nunzi, J.-M. *Appl. Phys. Lett.* **2006**, *89*, 213506. (b) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119–1122. (c) Lindner, S. M.; Hüttner, S.; Chiche, A.; Thelakkat, M.; Krausch, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 3364–3368. (d) Foster, S.; Finlayson, C. E.; Keivanidis, P. E.; Huang, Y.-S.; Hwang, I.; Friend, R. H.; Otten, M. B. J.; Lu, L.-P.;

Schwartz, E.; Nolte, R. J. M.; Rowan, A. E. *Macromolecules* **2009**, *42*, 2023–2030.

(5) (a) Ruiz Delgado, M. C.; Kim, E.-G.; da Silva Filho, D. A.; Bredas, J.-L. *J. Am. Chem. Soc.* **2010**, *132*, 3375–3387. (b) Vura-Weis, J.; Ratner, M. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2010**, *132*, 1738–1739.

(6) (a) Zhao, H.-M.; Pfister, J.; Settels, V.; Renz, M.; Kaupp, M.; Dehm, V. C.; Würthner, F.; Fink, R. F.; Engels, B. *J. Am. Chem. Soc.* **2009**, *131*, 15660–15668. (b) Gregg, B. A.; Kose, M. E. *Chem. Mater.* **2008**, *20*, 5235–5239.

(7) (a) Kasha, M. *Spectroscopy of the Excited State*; Plenum Press: New York, 1976. (b) Craig, D. P.; Walmsley, S. H. *Excitons in Molecular Crystals*: W. A. Benjamin, Inc.: New York, 1968.

(8) (a) Klebe, G.; Graser, F.; Haedicke, E.; Berndt, J. *Acta Crystallogr, Sect. B* **1989**, *B45*, 69–77. (b) Liu, S. G.; Sui, G.; Cormier, R. A.; Leblanc, R. M.; Gregg, B. A. *J. Phys. Chem. B* **2002**, *106*, 1307–1315. (c) Würthner, F.; Bauer, C.; Stepanenko, V.; Yagai, S. *Adv. Mater.* **2008**, *20*, 1695–1698. (d) Ghosh, S.; Li, X.-Q.; Stepanenko, V.; Würthner, F. *Chem.—Eur. J.* **2008**, *14*, 11343–11357. (e) Yagai, S.; Seki, T.; Karatsu, T.; Kitamura, A.; Würthner, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 3367–3371. (f) Mizuguchi, J.; Hino, K.; Tojo, K. *Dyes Pigm.* **2005**, *70*, 126–135.

(9) (a) Balakrishnan, K.; Datar, A.; Oitker, R.; Chen, H.; Zuo, J.; Zang, L. *J. Am. Chem. Soc.* **2005**, *127*, 10496–10497. (b) Balakrishnan, K.; Datar, A.; Naddo, T.; Huang, J.; Oitker, R.; Yen, M.; Zhao, J.; Zang, L. *J. Am. Chem. Soc.* **2006**, *128*, 7390–7398. (c) Datar, A.; Balakrishnan, K.; Yang, X.; Zuo, X.; Huang, J.; Oitker, R.; Yen, M.; Zhao, J.; Tiede, D. M.; Zang, L. *J. Phys. Chem. B* **2006**, *110*, 12327–12332.

(10) (a) Briseno, A. L.; Mannsfeld, S. C. B.; Reese, C.; Hancock, J. M.; Xiong, Y.; Jenekhe, S. A.; Bao, Z.; Xia, Y. *Nano Lett.* **2007**, *7*, 2847–2853. (b) Oh, J. H.; Lee, H. W.; Mannsfeld, S.; Stoltenberg, R. M.; Jung, E.; Jin, Y. W.; Kim, J. M.; Yoo, J.-B.; Bao, Z. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 6065–6070.

(11) (a) Galbiati, E.; Zoppo, M. D.; Tieghi, G.; Zerbi, G. *Polymer* **1993**, *34*, 1806–1810. (b) Hesse, S.; Suhm, M. A. *Phys. Chem. Chem. Phys.* **2009**, *11*, 11157–11170.

(12) Glaser, R. *J. Org. Chem.* **2001**, *66*, 771–779.

(13) (a) Snyder, R. G.; Maroncelli, M.; Qi, S. P.; Strauss, H. L. *Science* **1981**, *214*, 188–90. (b) Boese, R.; Weiss, H.-C.; Bläser, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 988–992.