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Citation for final published version:

Wu, Yi-Lin, Bobbitt, N. Scott, Logsdon, Jenna L., Powers-Riggs, Natalia E., Nelson, Jordan N., Liu, Xiaolong, Wang, Timothy C., Snurr, Randall Q., Hupp, Joseph T., Farha, Omar K., Hersam, Mark C. and Wasielewski, Michael R. 2018. Tunable crystallinity and charge transfer in two-dimensional G-quadruplex organic frameworks. *Angewandte Chemie International Edition* 57 (15), pp. 3985-3989. 10.1002/anie.201800230 file

Publishers page: <http://dx.doi.org/10.1002/anie.201800230>
<<http://dx.doi.org/10.1002/anie.201800230>>

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Tunable Crystallinity and Charge Transfer in Two-Dimensional G-Quadruplex Organic Frameworks

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Abstract: DNA G-quadruplex structures were recently discovered to provide reliable scaffolding for two-dimensional organic frameworks due to the strong hydrogen-bonding ability of guanine. Herein, 2,7-diaryl pyrene building blocks with high HOMO energies and large optical gaps are incorporated into G-quadruplex organic frameworks. The adjustable substitution on the aryl groups provides an opportunity to elucidate the framework formation mechanism; molecular non-planarity is found to be beneficial for restricting interlayer slippage, and the framework crystallinity is highest when intermolecular interaction and non-planarity strike a fine balance. When guanine-functionalized pyrenes are co-crystallized with naphthalene diimide, charge-transfer (CT) complexes are obtained. The photophysical properties of the pyrene-only and CT frameworks are characterized by UV/Vis and steady-state and time-resolved photoluminescence spectroscopies, and by EPR spectroscopy for the CT complex frameworks.

Stacking of crystalline two-dimensional (2D) organic frameworks provides a unique way to associate organic chromophores in a face-to-face arrangement with a high degree of precision. In these materials, the 2D frameworks can be constructed by reversible covalent linkages (covalent organic frameworks, COFs)^[1] or hydrogen bonding^[2] to arrange the monomeric units into periodic arrays. Eclipsed stacking with minimal interlayer slippage is often found when polycyclic

aromatic hydrocarbons (PAHs) are incorporated. Distinguished from its 3D counterparts,^[3] such a topology not only maximizes the dispersion interaction but creates channels for guest incorporation in the void space^[4] (akin to seminal work on porous van der Waals organic crystals),^[5] provides regular sites for spin interaction,^[6] and allows efficient charge transport through the p-stacks,^[1a,4c,7] essential for the application of these crystalline organic assemblies for energy conversion processes. It is often assumed that the planar structure of PAHs is essential for optimal 2D framework stacking and thereby good transport properties; in that regard, planar and sterically undemanding covalent linkages of boronate esters, imines, and triazines^[1c, 8] or non-covalent multi-valent hydrogen bonding motifs^[2b] are typically paired with PAHs to create 2D organic frameworks.

Inspired by the strong and precise hydrogen-bonding ability of DNA nucleobases, we demonstrated recently that electron-deficient naphthalene diimide (NDI) and perylene diimide (PDI) can be functionalized by electron-rich guanines to afford G-quadruplex organic frameworks (GQFs).^[9] In these materials, the extended 2D tetragonal grids are constructed from hydrogen-bonded guanine cyclic tetramers (G-quartets).^[10] Photoinduced electron transfer takes place from the covalently linked donor (guanine) to the photo-excited acceptors (NDI or PDI), ensuring efficient charge separation. The well-ordered and segregated donor/acceptor domains enable facile hole/electron transport as evidenced by transient optical and microwave conductivity measurements. To modulate the electronic properties of GQFs, in this work we introduce linearly disubstituted 2,7-diaryl pyrene as the GQF building block. Pyrene (Pyr) derivatives are chosen for their wide optical band gaps and high-lying HOMOs, providing a platform for interacting with electron acceptors for photoenergy conversion. By virtue of their facile synthesis, the formation mechanism for GQFs is elucidated as a function of the detailed geometry of their PAH building blocks. Furthermore, the size similarity and electronic complementarity of the Pyr and NDI moieties were exploited to probe their electronic interaction in the strong coupling regime, where the donor and acceptor form charge-transfer (CT) complexes in the GQF.

Similar to the previously reported synthetic strategy for G₂PhNDI,^[9] solid aggregates of G₂-Linker-Pyr were prepared from the tert-butyloxycarbonyl (Boc) substituted precursors (Linker = phenyl (Ph), tolyl (Tol), p-xylyl (pXy), and m-xylyl (mXy), Scheme 1). The degree of crystallinity of these materials varies unexpectedly to a great extent across the series. Similar to G₂PhNDI,^[9] solids of G₂TolPyr and

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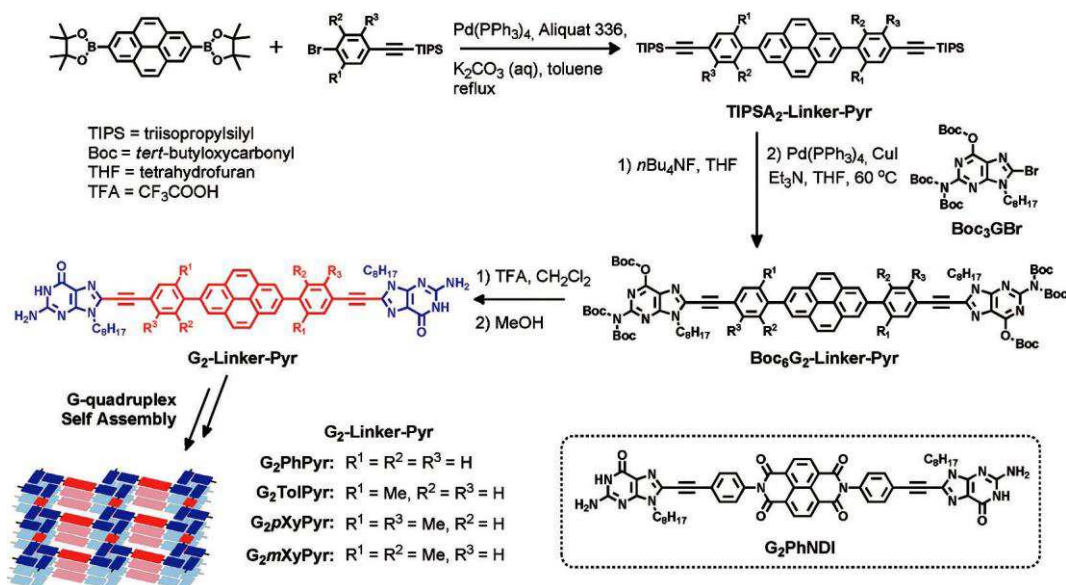
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Scheme 1. Preparation of 2,7-diaryl pyrene-incorporated G-quadruplex organic frameworks.

G₂pXyPyr display sharp peaks at 2.58 and 3.58 in powder X-ray diffraction (PXRD) profiles, suggesting formation of GQFs with high crystallinity; however, rather weak diffraction intensities in the 2–48 region were observed for G₂PhPyr and G₂mXyPyr, indicating the amorphous nature of the latter two aggregates (Figure 1 a). This disparity in crystallinity also manifests itself in the mesoscale morphology and gas adsorption behavior. Scanning electron microscopy (SEM) shows that G₂TolPyr and G₂pXyPyr form rod-shape crystallites that assemble into spherical aggregates, whereas unstructured masses were observed for G₂PhPyr and G₂mXyPyr (Figure S4 in the Supporting Information). Moderate N₂ adsorption further supports the microporous superstructure in the Tol and pXy derivatives; on the other hand, negligible gas adsorption was detected for G₂mXyPyr (Figure 1 b).

Although 2,7-diaryl pyrenes are isostructural to N,N-diphenyl NDI, the different degree of crystallinity observed for G₂-Linker-Pyr indicates that the ability to form predictable hydrogen-bonded networks alone is not the only requirement for 2D framework formation. Closer scrutiny of the isolated molecular structure indicated that the dihedral angle f between the Ph-Pyr moieties is 328,^[11] much smaller than that between Ph-NDI ($f = 658$).^[12] This suggests that the small f (Ph-Pyr) angle may allow interlayer slippage between G-quartet units which prohibits the formation of an extended 2D domain. With the methyl substitution, the dihedral angles increase to f (Tol-Pyr) = 558, as determined by the single crystal X-ray structure of the synthetic intermediates (Figure S1), reaching the value for f (Ph-NDI). Since these G₂-Linker-Pyr molecules form well-ordered frame-

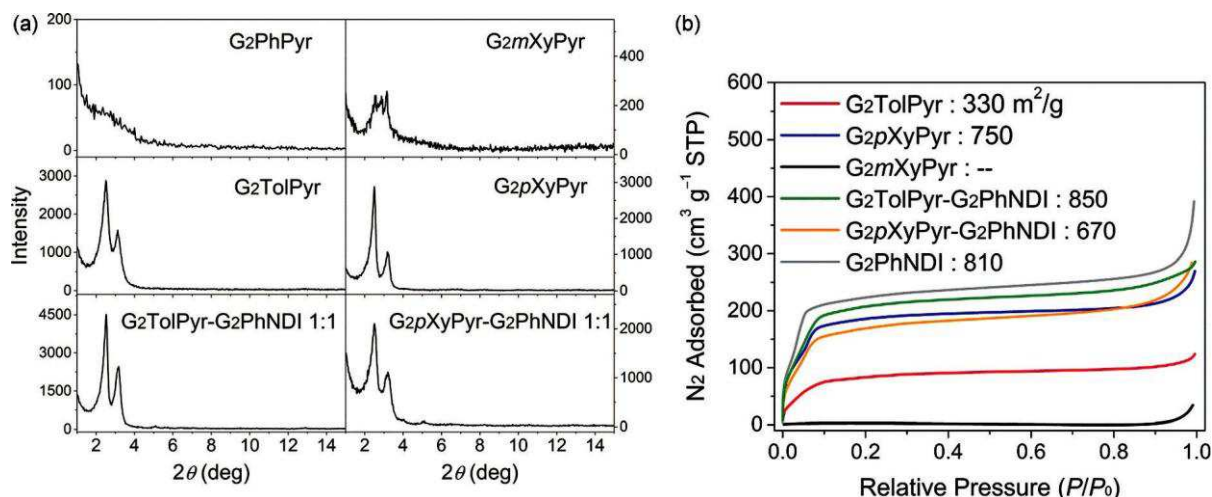


Figure 1. a) Powder X-ray diffraction patterns of G₂-Linker-Pyr and the charge-transfer complexes prepared from a 1:1 mixture of G₂PhNDI and G₂-Linker-Pyr. Full-width at half-maximum of the peak at $2\theta = 2.58$ is 0.368 for G₂TolPyr, 0.258 for G₂pXyPyr, 0.278 for G₂TolPyr-G₂PhNDI, 0.318 for G₂pXyPyr-G₂PhNDI, and 0.198 for G₂PhNDI.^[9] b) N₂ adsorption isotherms measured at 77 K; the Brunauer-Emmett-Teller (BET) area of each material is given (see Figure S10 for the desorption isotherms).

works while G₂PhPyr does not, we hypothesized that the non-planarity creates docking sites for each chromophore/G-quartet unit to stack in registry, a similar idea and observation reported recently by Bein and co-workers.^[13] The much larger $f(\text{mXy-Pyr}) = 828$, however, make the mXy and Pyr moieties orthogonal to one another and prevent the stacking interaction.

To test this hypothesis, the computed interaction energy between two G-quartet layers, defined as [E(2 G-quartets at point r) @ 2.0 E(1 G-quartet)], with various extents of interlayer slippage are compared for G₂-Linker-Pyr, and we focus on G₂PhPyr and G₂TolPyr in the discussion below (Figure 2). In these calculations, the molecular structures of the G-quartet units, optimized at the level of PBE-D3/Def2SVP,^[14] were held static and the two layers were translated laterally in the x and y directions at a constant interlayer distance (z). The energy-minimum interlayer distances for two eclipsed layers (Dx = Dy = 0) were chosen as the z value to perform the interaction-energy scan in the x,y directions (Figure S7). The energy surfaces covering Dx = Dy = 3 Å were calculated using a Lennard-Jones plus Coulomb potential with Lennard-Jones parameters taken from UFF^[15] and partial charges calculated with the charge equilibration method (QEq),^[16] and a single quadrant was examined by the same DFT method used for the monomers.

G-quartet layers of G₂TolPyr were found to display a narrow region of moderate interaction, whereas a wide and strongly attractive area over Dx,y : 1.5 Å is available for G₂PhPyr to p-stack. In other words, the relative interlayer slippage for the G₂TolPyr G-quartet units in the course of framework formation is mutually restricted by the adjacent layers due to the tolyl groups rotating out of the mean plane of the aromatic moieties, and thus networks of every stacked

G-quartet unit extend in 2D in a regular manner. For G₂PhPyr, however, such a restriction is absent and no long-range ordering was observed by PXRD, even though the binding energy for G₂PhPyr at the origin is stronger than that for G₂TolPyr. The attractive interaction is primarily dispersive in nature, as suggested by the similar results from the PBE-D3, UFF + QEq, and UFF calculations (Figure S8). G₂ mXyPyr has a much larger dihedral angle, which results in a repulsive interaction between the layers and prohibits framework formation (Figure S9).

The large interlayer spacing for G₂TolPyr suggested computationally may seem counterintuitive for p-stacked organic frameworks, which often display a distance around 3.5 Å. Although we were unable to obtain a transmission electron microscopy (TEM) image to confirm such a lattice dimension, for G₂pXyPyr, we found a set of distinct selected area electron diffraction (SAED) patterns corresponding to a d-spacing of 4.5 : 0.2 Å (Figure S12). This length scale is likely related to the interlayer distance found computationally (4.88 Å by force field calculations) and similar to what was observed in COFs composed of core-twisted building blocks (4.6–4.7 Å).^[13b, 17] The resemblance between these interlayer distances supports the credibility of the computational analysis; furthermore, it indicates that the strong interlayer interaction energy is not the most important factor for crystalline framework formation, and out-of-plane twisting can in fact modulate the interaction energy, in turn allowing the correction of structural defects, and encouraging molecules to stack in registry.

The similar framework-forming propensity between the present cases and G₂PhNDI permits co-crystallization of G₂TolPyr-G₂PhNDI and G₂pXyPyr-G₂PhNDI from an equimolar mixture of G₂TolPyr or G₂pXyPyr and G₂PhNDI. The resultant hetero-GQFs display similar PXRD patterns and BET areas to their respective homo-GQFs (Figure 1). When a mixture of G₂PhPyr and G₂PhNDI was used, the Pyr- and NDI-rich phases segregated (Figure S5), indicating the self-interaction between Pyr moieties is too strong to allow NDI to template the framework growth. Interestingly, while sharper PXRD peaks and a higher BET area were observed for the G₂pXyPyr homo-GQF than G₂TolPyr; for the hetero-GQFs, G₂TolPyr-G₂PhNDI shows higher BET area and smaller PXRD width compared to G₂pXyPyr-G₂PhNDI. These results indicate that the size of the substituents and the degree of non-planarity dictate the crystallinity of the resultant material in a non-trivial fashion. A fine balance between the steric repulsion and p-stacking is required for high regularity.

In the solid state, G₂-Linker-Pyr features broad visible absorption covering 300–480 nm. Their photo-luminescence spectra as well as lifetimes (ca. 1 ns) of these solids appear to be similar to those of their corresponding monomers in solution, suggesting the guanine-origin emission^[18] due to fast energy transfer and a weak tendency toward excimer formation for 2,7-diarylpyrene derivatives (Figure 3 a and Supporting Information Section 4).^[19] New visible absorption

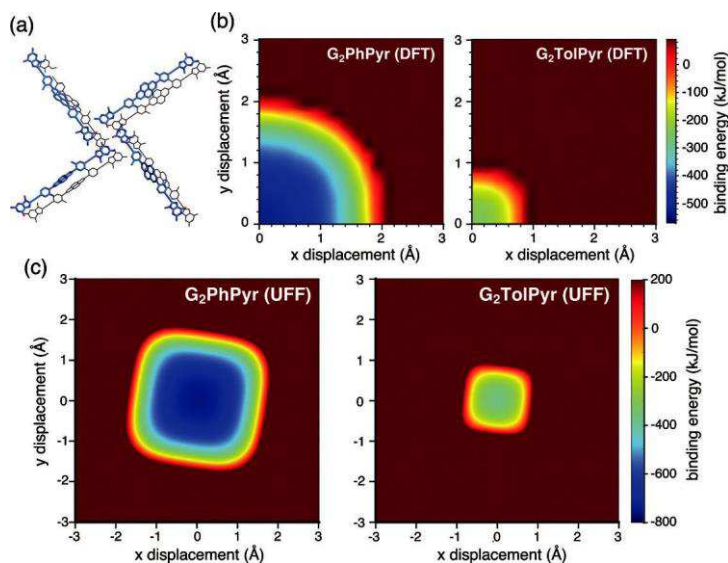


Figure 2. a) Schematic representation of two G-quartet layers (one shown in blue and one in gray) used in the calculations of the interaction energy maps. b) Interaction energy map calculated at the level of PBE-D3/Def2SVP at $z = 3.90$ Å for G₂PhPyr and 5.01 Å for G₂TolPyr. c) Interaction energy map calculated at the level of UFF + QEq charges at $z = 3.93$ Å for G₂PhPyr and 5.18 Å for G₂TolPyr.

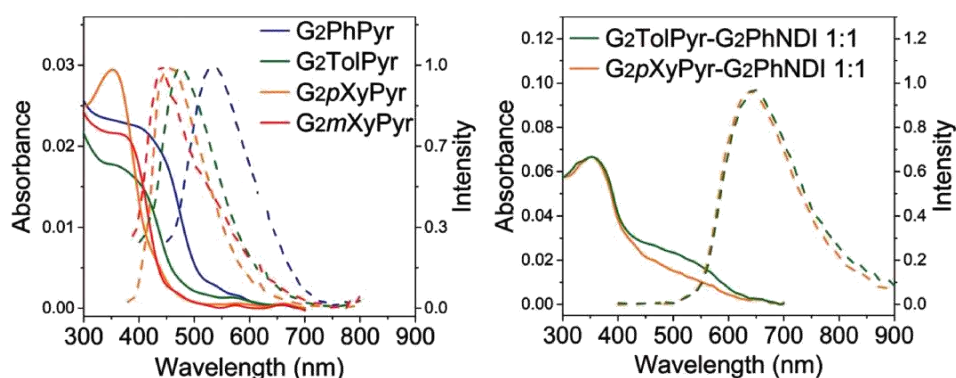


Figure 3. Absorption (solid lines) and photoluminescence (dashed lines) spectra of solid samples of a) G₂-Linker-Pyr or b) G₂-Linker-Pyr G₂PhNDI.

(ca. 540 nm) and emission (ca. 650 nm) bands were observed for the hetero-GQFs of G₂TolPyr-G₂PhNDI and G₂pXyPyr-G₂PhNDI. The photoluminescence lifetimes are extended to approximately 4.5 ns, and their red appearance is reminiscent of the charge-transfer (CT) absorption of Pyr-NDI cyclophanes^[20] and concentrated solutions or crystals containing these two molecules.^[21] The CT nature is corroborated by range-separated TD-DFT calculations at the LRC-wPBEh/6-31G(d)//wB97X-D/6-31G(d) level of theory (Pyr-NDI p-spacing ca. 3.5 Å),^[22] which suggest that the low-energy transition is a CT band and significant electron density shifts from Pyr to NDI upon excitation (Figure S13). The CT character is further supported by differences in FT-IR spectra; for example, the carbonyl stretching at 1720 cm⁻¹ for G₂PhNDI is not observed for the hetero-GQFs (Figure S14). Such changes can be attributed to broadening and shifting of this peak to a lower frequency, consistent with weakening of this vibration mode due to accepting extra electron density.

Interestingly, a weak EPR spectrum was observed for these hetero-GQFs (Figure S15). The field-modulated continuous-wave EPR spectra measured at approximately 9.5 GHz show a single first-derivative signal centered at g

2 containing contributions from both PyrC⁺ and NDIC[•], where the hyperfine coupling is unresolved owing to orientation averaging in the powder samples. Using pulse-EPR electron spin echo spectroscopy at around 34 GHz, the integrated Hahn echo intensity yields the spectrum showing two resolved signals of PyrC⁺ and NDIC[•] at g 2.0025 and 2.0031, respectively,^[23] indicating that charge separation occurs within the hetero-GQF. Although electron-density shifts in CT complexes do not usually result in a full electron transfer and EPR activity,^[24] such signals have been observed in metal-organic frameworks (MOF)^[25] and CT complexes of small organic molecules having alternating donor-acceptor p stacks.^[26] To our knowledge, the present examples are the first demonstration of isolable 2D organic frameworks, where the intrinsic p-stacking in the structure can be exploited for CT complex formation.^[27]

In summary, we show herein that the very strong attractive interlayer interaction between planar PAH molecules may actually prohibit the formation of extended regular 2D frameworks. Some degree of non-planarity in the molec-

ular building blocks can provide slippage restriction and reduce the interlayer interaction to an extent favorable for error correction during framework formation. Applying this methodology, GQFs constituting Pyr-only or Pyr-NDI building blocks were prepared. The combination of the large optical gap and high lying HOMO energy implies possible application of Pyr GQFs as strong photoreductants for photocatalytic reactions. Given the non-centrosymmetric nature of the G-quartet

units, the CT GQF may be ferroelectric.^[28] Further electron conductivity and magnetic susceptibility studies are warranted.

Acknowledgements

This work was supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, DOE under grant Nos. DE-FG02-99ER14999 (M.R.W.), DE-FG02-17ER16362 (R.Q.S. and O.K.F.), and DE-FG02-87ER13808 (J.T.H.). J.L.L. and N.E.P.-R. were supported by an NSF Graduate Research Fellowship. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. This research was supported in part through the computational resources and staff contributions provided for the Quest high performance computing facility at North-western University which is jointly supported by the Office of the Provost, the Office for Research, and Northwestern University Information Technology.

Conflict of interest

The authors declare no conflict of interest.

Keywords: charge-transfer complexes · crystal engineering · G-quadruplexes · organic frameworks · self-assembly

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