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Supramolecular Assemblies for Electronic Materials

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Abstract: We present here a synergy between organic electronics and supramolecular chemistry, in which a host–guest complex is designed to function as an efficacious electronic material. Specifically, the non-covalent recognition of a fullerene, phenyl-C$_{61}$-butyric acid methyl ester (**PC$_{61}$BM**), by our alternating perylene diimide (**P**)–bithiophene (**B**) conjugated macrocycle (**PBPB**) results in a greater than five-fold enhancement in electron mobility, relative to the macrocycle alone. Characterisation and quantification of the binding of fullerenes by host **PBPB** is provided alongside evidence for intermolecular electronic communication within the host–guest complexes.

Here we study a host–guest complex as an electronic material and reveal a synergy between supramolecular chemistry and organic electronics. Typically host–guest complexes are designed from pieces that have drastically different energies for their frontier orbitals[1–5] that can prevent the smooth transfer of charge through the material. In this study we have married two electron transporting materials that have similar LUMO levels, a PDI-based conjugated macrocycle and a fullerene. Fullerenes are ubiquitous electron accepting[6] and transporting materials.[7–11] PDI-based conjugated macrocycles are a new class of organic electronic material that possess several advantages as n-type materials including: tuneable electronic properties; extensive π-conjugation; and shape persistent cavities that facilitate guest incorporation and sensing.[12,13] Indeed, conjugated macrocycles form the electron-transporting material in organic field effect transistors (OFETs),[14–16] photodetectors,[17] and photovoltaics.[14] Here we utilize the shape and functional group complementarity between these two electronic components to form a robust host–guest complex that can be readily processed to generate a superior electronic material. The macrocycle component has an alternating diphenyl-PDI (**P**) and bithiophene (**B**) structure, **PBPB** (Figure 1).[12] **PBPB** is an ideal material to bind to fullerenes.[18–26] It possesses a large, curved nanospace interior,[18,22,24,27,28] which is lined with Lewis basic sulfur atoms for (n)–π interactions.[29] We thereby investigate the supramolecular chemistry of **PBPB** and find it binds a variety of fullerenes with association constants (K_a), of up to 9,278 M^{-1}. Molecular recognition is concomitant with significant intermolecular electronic communication between the two components. Therefore, we cast the complex of **PBPB** and fullerene phenyl-C$_{61}$-butyric acid methyl ester (**PC$_{61}$BM**) into thin films and make OFETs from them. We find the supramolecular complex (**[PBPB] ⊃ [PC$_{61}$BM]**) improves material processability and shows a greater than five-fold enhancement in electron mobility relative to the neat films of **PBPB**.

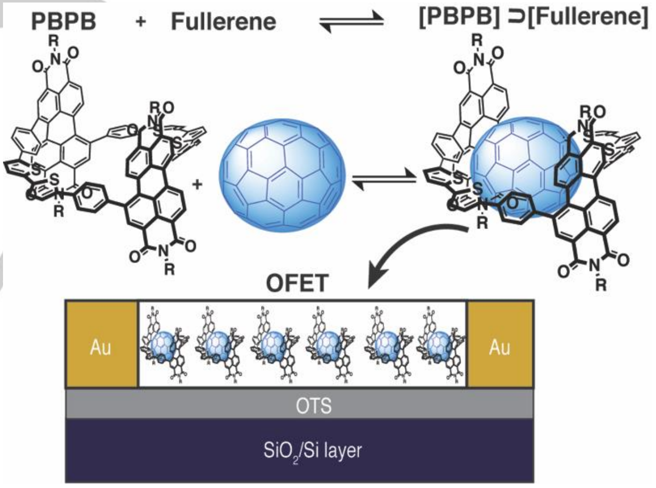

Figure 1. Molecular recognition between macrocycle (**PBPB**) and fullerene (**PC$_{61}$BM**, **C$_{70}$** or **C$_{60}$**) forms a supramolecular complex, [**PBPB**] ⊃ [**Fullerene**]. The [**PBPB**] ⊃ [**PC$_{61}$BM**] complexes are used in the active layer of OFET devices to enhance electron mobility. (R = CH(C$_5$H$_{11}$)$_2$).

We initially investigate the supramolecular chemistry of macrocycle **PBPB** via host–guest binding studies with fullerenes **C$_{60}$** and **C$_{70}$** as well as **PC$_{61}$BM**. We monitor the formation of a supramolecular complex between **PBPB** and these nanocarbons in d$_8$-toluene solution using NMR spectroscopy (SI section 6). Specifically, ^{1}H and ^{13}C NMR titration experiments[30] show *three* features indicative of supramolecular complex formation with each guest: 1) π–π interactions between aromatic rings of the PDI and fullerene, 2) S:–π interactions originating from the bithiophene heterocycles to the fullerene, and 3) CH–π interactions between the alkyl chains and the fullerene (Figure 2c).[31]

Over the course of the titration, we observe the largest downfield shifts of phenyl aromatic protons H_d and H_e ($\Delta\delta$ = 0.18 ppm, Figure 2a,c and Figures S6.1 – S6.3), indicative of intermolecular π–π aromatic stacking interactions between fullerene guest and aromatic belt of the **PBPB** host.[32] This complex was supported by upfield shifts of the fullerene resonances in the ^{13}C NMR spectrum, consistent with a ring current effect from the diamagnetic aromatic system of the macrocycle (Figures 2b,c, S6.9 and S6.10).[33] By contrast, the thiophene proton shift is much less pronounced ($\Delta\delta$ H_h = 0.02 - 0.05 ppm) since these protons are positioned outside the cavity (Figure 2c).[18] The flexible **PBPB** $CH(C_5H_{11})_2$ imide chains also undergo favourable CH–π interactions with the fullerene, as evidenced by the shift of methylene H_f and H_g signals. These signals are also split into four peaks of equally integrated intensity (*i.e.* H_f, H_g, $H_{f'}$, $H_{g'}$, Figure 2c and S6.6) since the difference between internal and external environments of **PBPB** is enhanced upon fullerene encapsulation. The steric and electronic role of the alkyl side chains was further highlighted by **C₇₀** being more than an order of magnitude weaker binder when aryl substituents (2,6-diisopropyl phenyl) were used at the imide positions instead of the alkyl chains (*aryl*-**PBPB**,[34] K_a = 591 ± 6 M^{-1}, Figure S6.4).

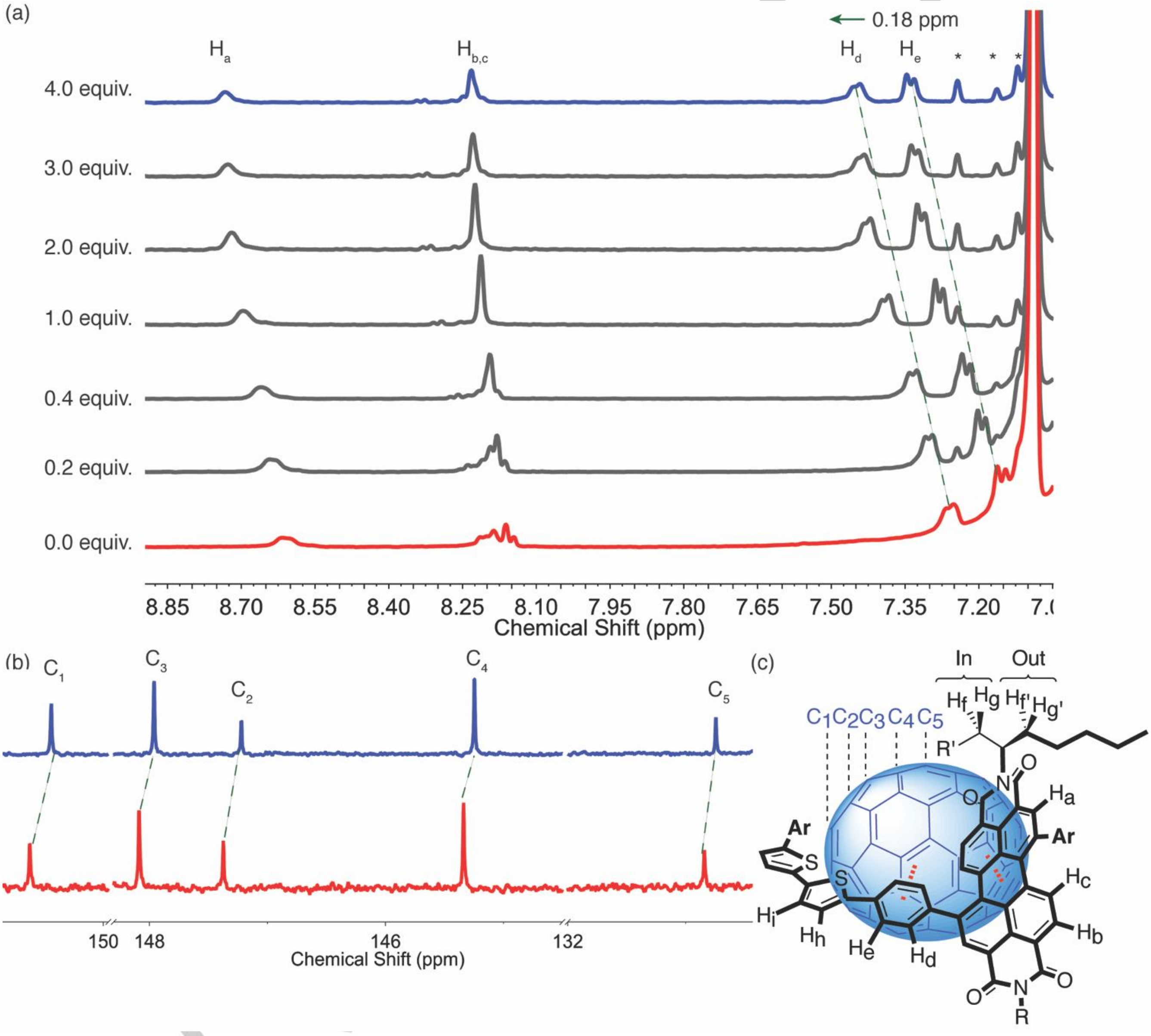

Figure 2. (a) ^{1}H NMR spectra from the titration of **C₇₀** fullerene guest into a 0.5 mM host solution of **PBPB**; (b) ^{13}C NMR spectra showing evidence of **PBPB** complexation of **C₇₀**; and (c) a schematic of [**PBPB**] ⊃ [**C₇₀**] with labelled nuclei. (Start point = red, end point = blue, ^{1}H = 500 MHz, ^{13}C = 125 MHz, d_8-toluene, 298 K, * = solvent and its satellites, R = $CH(C_5H_{11})_2$, R' = C_4H_9)

We quantified the association between the fullerene and **PBPB** using Bindfit.[35] We monitored the H_e aryl proton signals because they produced the greatest shift (Figure 2a and S6.1 – S6.3). Job's plot analyses, non-sigmoidal residues, and low fitting covariances indicated a 1:1 host–guest stoichiometric binding model (SI, section 7). The association constant for **C_{70}** was over four times that of **C_{60}**, (K_a = 9,278 ± 649 M^{-1} *vs.* 2,119 ± 21 M^{-1}).[36] The enhanced binding of **C_{70}** suggests the ellipsoidal aromatic cavity of **PBPB** provides a better size and shape complementarity with this "rugby-ball" shaped fullerene guest (Figure 2c). This binding preference was also confirmed by a competition experiment between **C_{60}** and **C_{70}** using ^{13}C NMR spectroscopy (Figure S6.11).

Strong binding of fullerene **$PC_{61}BM$** was also observed (K_a = 1,336 ± 27 M^{-1}), despite the steric bulk arising from covalent functionalisation of the carbon cage.[36] The existence of supplementary intermolecular π–π aromatic stacking interactions for its recognition are indicated by downfield shifts of protons on the exohedral phenyl ring of the **$PC_{61}BM$** (Figure S6.3). In contrast to the case of **PBPB**, weak or negligible fullerene binding was observed with analogous PDI-based hosts containing either a larger cavity (**DBDB**, Figure S6.8)[15] or acyclic framework (*acyclic*-**PDI**, Figure S6.7).[14]

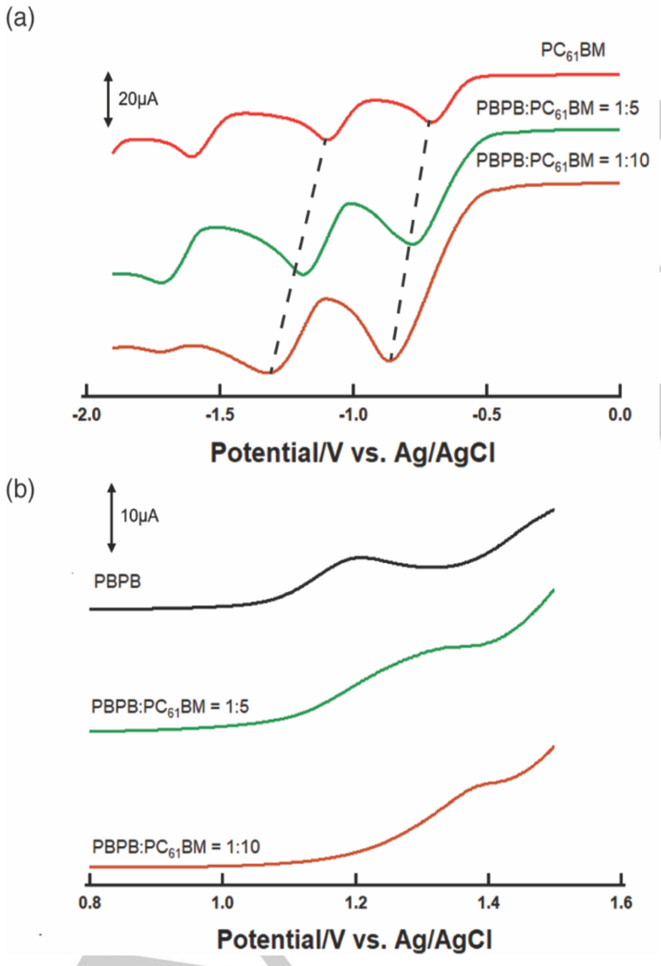

Figure 3. Electrochemical titrations showing cathodic and anodic shifts in the respective a) fullerene reduction, and b) macrocycle oxidation peaks upon formation of complex [**PBPB**] ⊃ [**$PC_{61}BM$**].

We used mass spectrometry (ESI), to further characterise the fullerene recognition properties of macrocycle **PBPB**. Signals corresponding to the complex [**PBPB**] ⊃ [**Fullerene**] were found from analysis of each of the NMR titration solutions at their end point (SI, section 4). Comparatively weaker peaks for a 1:2 host–guest complex were also observed (Figure S4.4), however, under the more competitive conditions of the solution phase, this second association is too weak to be observed by ^{1}H NMR spectroscopy. A further indication of the strength of these complexes was provided by collision induced dissociation MS/MS experiments; large collision energies (~80 eV) were required to observe peaks for the individual components (Figures S4.1 – 4.3). To put this into context, the de-threading of a hydrogen bond-based pseudorotaxane interpenetrated assembly has been reported at a collision energy of 40 eV.[37]

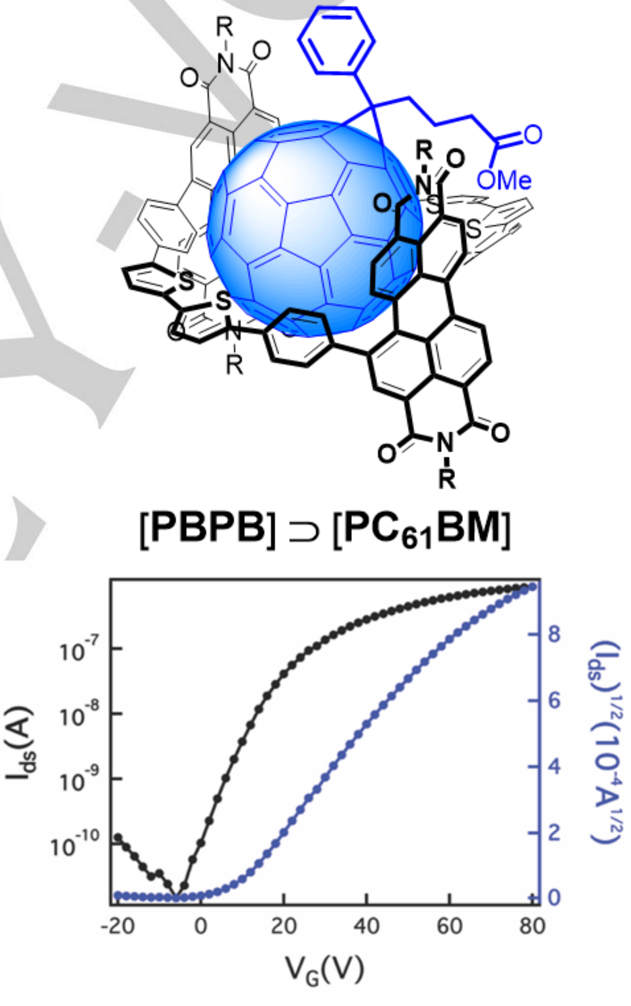

Figure 4. Transfer curve for OFET device with [**PBPB**] ⊃ [**$PC_{61}BM$**] complex as the active layer. Device current (left axis, black) and square root of current (right axis, blue) measured as a function of gate voltage at a constant source-drain voltage (80 V).

Electrochemical studies provided insight into intermolecular electronic communication within the complex [**PBPB**] ⊃ [**$PC_{61}BM$**]. The titration of **$PC_{61}BM$** into **PBPB** induced a cathodic shift of up to 230 mV of the **$PC_{61}BM$** fullerene reduction waves (Figure 3a and SI, section 2). This was concomitant with a 200 mV anodic shift of the **PBPB** macrocycle oxidation wave (Figure 3b). Therefore, while both components are categorised as n-type materials (SI section 2), there is partial ground state charge transfer from macrocycle host to fullerene guest.[38] In fact, the anodic perturbation of macrocycle **PBPB** (200 mV) is much larger than other reported oxidisable fullerene hosts (20 – 40 mV).[21,39] The strong electronic communication between aromatic surfaces is due to their tight supramolecular association, occurs without the need for them to be covalently bonded together.[40] As such, the ground state interaction within [**PBPB**] ⊃ [**PC$_{61}$BM**] raises the LUMO energy of **PC$_{61}$BM** and lowers the HOMO of **PBPB**.

Electronic absorption (UV-Vis) and fluorescence emission titrations also support this intermolecular electronic communication within the host–guest complexes (SI, section 8). Fullerene binding caused a decrease in intensity of the lowest energy absorption band of **PBPB**, concomitant with an increase in absorption at longer wavelengths (isosbestic point at $\lambda = 650$ nm, Figures S8.1 and 8.2).[41] Since the lowest energy absorption band of **PBPB** arises from a bithiophene to PDI transition,[12] the complex-induced spectroscopic perturbation occurs because the fullerene competes with the PDI units as an electron acceptor. Furthermore, significant quenching of **PBPB** fluorescence emission was observed upon guest recognition (Figure S8.3), indicative of intermolecular electronic communication via the excited state.[42]

Since **PBPB** and **PC$_{61}$BM** show strong electronic communication we sought to use the supramolecular complex as the active layer in an OFET device. Specifically, a layer of SiO_2 on a silicon wafer was used as a substrate to which Ti and Au were deposited as the bottom contact source and drain electrodes giving a channel width of 105 μm and length of 20 μm (Supporting Information, section 3). The electrodes were modified with 2,3,4,5,6-pentafluorothiophenol and the substrate with octadecyltrichlorosilane (OTS). We fabricated thin films of the supramolecular complex as the active layer of these devices by spin casting a solution of [**PBPB**] ⊃ [**PC$_{61}$BM**] from chloroform and annealing at 140 °C under an inert atmosphere. We compared the device performance of the supramolecular complex [**PBPB**] ⊃ [PC$_{61}$BM] to that from films comprising only **PBPB** or **PC$_{61}$BM**.

Figure 4 displays the current *vs.* applied gate voltages (transfer curves) for the [**PBPB**] ⊃ [**PC$_{61}$BM**] OFET device. We collected the data for these transfer curves using a source-drain voltage of 80 V while sweeping the gate voltage from - 20 V to 80 V (SI, section 3). We find the mobility of the complex [**PBPB**] ⊃ [**PC$_{61}$BM**] is over five times that of neat **PBPB**[14] (8.0×10^{-3} $cm^2/V{\bullet}s$ *vs*. 1.5×10^{-3} $cm^2/V{\bullet}s$)[43] and also greater than that of many of our previous PDI-based macrocycles.[14,15] The formation of the [**PBPB**] ⊃ [**PC$_{61}$BM**] complex and its strong electronic interaction between host and guest enhances the mobility of the material. An improvement in electrical conductivity has also been reported in single crystals comprised of a C_{60} fullerene bound within the cavity of a viologen-based cyclophane.[44]

It is also possible that thin film morphology is a contributing factor in enhancing electron mobility. We found that thin films of neat **PC$_{61}$BM** prepared under analogous conditions were non-conducting due to aggregation of the fullerene during the annealing process. While powder X-Ray diffraction revealed films of the individual components to be amorphous, modest crystalline features from the [**PBPB**] ⊃ [**PC$_{61}$BM**] complex film suggests this material is more ordered (Figure S5.1).

This study describes how the self-assembly of two n-type semiconductors generates an efficacious conducting material with enhanced electron mobility and thin film processability. Specifically, the sequestration of the fullerene guest **PC$_{61}$BM** by **PBPB** leads to an enhancement in OFET device performance relative to the empty host (Figure 1). Structural characterisation and quantification of supramolecular complexes is provided through ^1H and ^{13}C NMR spectroscopy and mass spectrometry. Evidence for strong intermolecular electronic communication between bithiophene donors of the macrocycle and the fullerene acceptor is seen in the electrochemistry, electronic absorption and fluorescence emission spectroscopies. Therefore, the geometric and electronic complementarity within these [**PBPB**] ⊃ [**PC$_{61}$BM**] complexes and their effect on film morphology, provide a combination of factors responsible for enhancing electron mobility in the new supramolecular material.

Acknowledgements

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Keywords: supramolecular chemistry • fullerenes • macrocycles • molecular electronics • organic semiconducting materials

[1] S. J. Kang, J. B. Kim, C.-Y. Chiu, S. Ahn, T. Schiros, S. S. Lee, K. G. Yager, M. F. Toney, Y.-L. Loo, C. Nuckolls, *Angew. Chem. Int. Ed.* **2012**, *51*, 8594–8597; *Angew. Chem*. **2012**, *124*, 8722-8725.

[2] Q. Huang, G. Zhuang, H. Jia, M. Qian, S. Cui, S. Yang, P. Du, *Angew. Chem. Int. Ed.* **2019**, *58*, 6244–6249; *Angew. Chem*. **2019**, *131*, 6310-6315.

[3] T. Hasobe, H. Imahori, P. V. Kamat, T. K. Ahn, S. K. Kim, D. Kim, A. Fujimoto, T. Hirakawa, S. Fukuzumi, *J. Am. Chem. Soc*. **2005**, *127*, 1216–1228.

[4] I. D. Tevis, W.-W. Tsai, L. C. Palmer, T. Aytun, S. I. Stupp, *ACS Nano* **2012**, *6*, 2032–2040.

[5] H. Imahori, M. Ueda, S. Kang, H. Hayashi, S. Hayashi, H. Kaji, S. Seki, A. Saeki, S. Tagawa, T. Umeyama, Y. Matano, K. Yoshida, S. Isoda, M. Shiro, N. V. Tkachenko, H. Lemmetyinen, *Chem. - A Eur. J.* **2007**, *13*, 10182–10193.

[6] L. Echegoyen, L. Echegoyen, *Acc. Chem. Res*. **1998**, *31*, 593–601.

[7] S. Iijima, *Nature* **1991**, *354*, 56–58.

[8] E. Castro, J. Murillo, O. Fernandez-Delgado, L. Echegoyen, *J. Mater. Chem. C* **2018**, *6*, 2635–2651.

[9] D. M. Guldi, B. M. Illescas, C. M. Atienza, M. Wielopolski, N. Martín, *Chem. Soc. Rev.* **2009**, *38*, 1587.

[10] M. A. Lebedeva, T. W. Chamberlain, A. N. Khlobystov, *Chem. Rev.* **2015**, *115*, 11301–11351.

[11] T. A. Barendt, I. Rašović, M. A. Lebedeva, G. A. Farrow, A. Auty, D. Chekulaev, I. V. Sazanovich, J. A. Weinstein, K. Porfyrakis, P. D.

Beer, *J. Am. Chem. Soc.* **2018**, *140*, 1924–1936.

[12] M. Ball, B. Fowler, P. Li, L. A. Joyce, F. Li, T. Liu, D. Paley, Y. Zhong, H. Li, S. Xiao, F. Ng, M. L. Steigerwald, C. Nuckolls, *J. Am. Chem. Soc.* **2015**, *137*, 9982–9987.

[13] M. Ball, B. Zhang, Y. Zhong, B. Fowler, S. Xiao, F. Ng, M. Steigerwald, C. Nuckolls, *Acc. Chem. Res.* **2019**, *52*, 1068–1078.

[14] M. Ball, Y. Zhong, B. Fowler, B. Zhang, P. Li, G. Etkin, D. W. Paley, J. Decatur, A. K. Dalsania, H. Li, S. Xiao, F. Ng, M. L. Steigerwald, C. Nuckolls, *J. Am. Chem. Soc.* **2016**, *138*, 12861–12867.

[15] M. L. Ball, B. Zhang, Q. Xu, D. W. Paley, V. C. Ritter, F. Ng, M. L. Steigerwald, C. Nuckolls, *J. Am. Chem. Soc.* **2018**, *140*, 10135–10139.

[16] B. Zhang, R. Hernández Sánchez, Y. Zhong, M. Ball, M. W. Terban, D. Paley, S. J. L. Billinge, F. Ng, M. L. Steigerwald, C. Nuckolls, *Nat. Commun.* **2018**, *9*, 1957.

[17] B. Zhang, M. Tuan Trinh, B. Fowler, M. Ball, Q. Xu, F. Ng, M. L. Steigerwald, X.-Y. Zhu, C. Nuckolls, Y. Zhong, *J. Am. Chem. Soc.* **2016**, *138*, 16426–16431.

[18] S. Toyota, E. Tsurumaki, *Chem. - A Eur. J.* **2019**, *25*, 6878–6890.

[19] T. Iwamoto, Y. Watanabe, T. Sadahiro, T. Haino, S. Yamago, *Angew. Chem. Int. Ed.* **2011**, *50*, 8342–8344; *Angew. Chem*. **2011**, *123*, 8492-8494.

[20] Y. Xu, S. Gsänger, M. B. Minameyer, I. Imaz, D. Maspoch, O. Shyshov, F. Schwer, X. Ribas, T. Drewello, B. Meyer, M. von Delius, *J. Am. Chem. Soc.* **2019**, *141*, 18500–18507.

[21] T. A. Barendt, W. K. Myers, S. P. Cornes, M. A. Lebedeva, K. Porfyrakis, I. Marques, V. Félix, P. D. Beer, *J. Am. Chem. Soc.* **2019**, DOI 10.1021/jacs.9b10929.

[22] X. Lu, T. Y. Gopalakrishna, Y. Han, Y. Ni, Y. Zou, J. Wu, *J. Am. Chem. Soc.* **2019**, *141*, 5934–5941.

[23] S. Ferrero, H. Barbero, D. Miguel, R. García-Rodríguez, C. M. Álvarez, *J. Org. Chem.* **2019**, *84*, 6183–6190.

[24] S. Selmani, D. J. Schipper, *Chem. – A Eur. J.* **2019**, *25*, 6673–6692.

[25] F. Würthner, C. R. Saha-Möller, B. Fimmel, S. Ogi, P. Leowanawat, D. Schmidt, *Chem. Rev.* **2016**, *116*, 962–1052.

[26] Y. Shi, K. Cai, H. Xiao, Z. Liu, J. Zhou, D. Shen, Y. Qiu, Q.-H. Guo, C. Stern, M. R. Wasielewski, F. Diederich, W. A. Goddard III, J. F. Stoddart, *J. Am. Chem. Soc.* **2018**, *140*, 13835–13842.

[27] D. Canevet, E. M. Pérez, N. Martín, *Angew. Chem. Int. Ed.* **2011**, *50*, 9248–9259; *Angew. Chem*. **2011**, *123*, 9416-9427.

[28] E. M. Pérez, N. Martín, *Chem. Soc. Rev.* **2008**, *37*, 1512.

[29] H. Shimizu, J. D. Cojal González, M. Hasegawa, T. Nishinaga, T. Haque, M. Takase, H. Otani, J. P. Rabe, M. Iyoda, *J. Am. Chem. Soc.* **2015**, *137*, 3877–3885.

[30] For titration experiments, up to ten equivalents of fullerene guest were added into a 0.5 mM solution of **PBPB** host.

[31] The ^{1}H NMR spectrum of macrocycle **PBPB** in toluene is independent of concentration in the range of the titration experiment (0.5 – 0.2 mM, Figure S6.5). Some macrocycle peaks are doubled due to the existence of diastereomers.[12]

[32] M. Gallego, J. Calbo, R. M. Krick Calderon, P. Pla, Y.-C. Hsieh, E. M. Pérez, Y.-T. Wu, E. Ortí, D. M. Guldi, N. Martín, *Chem. - A Eur. J.* **2017**, *23*, 3666–3673.

[33] D. Sun, F. S. Tham, C. A. Reed, L. Chaker, M. Burgess, P. D. W. Boyd, *J. Am. Chem. Soc*. **2000**, *122*, 10704–10705.

[34] The SI (section 1) contains the synthesis and characterisation for *aryl*-**PBPB**.

[35] Bindfit: http://supramolecular.org.

[36] See Supporting Information, section 7 for further details of residuals and Job's plot analysis.

[37] H. V. Schröder, J. M. Wollschläger, C. A. Schalley, *Chem. Commun.* **2017**, *53*, 9218–9221.

[38] L. Moreira, J. Calbo, R. M. Krick Calderon, J. Santos, B. M. Illescas, J. Aragó, J.-F. Nierengarten, D. M. Guldi, E. Ortí, N. Martín, *Chem. Sci.* **2015**, *6*, 4426–4432.

[39] M. Takeda, S. Hiroto, H. Yokoi, S. Lee, D. Kim, H. Shinokubo, *J. Am. Chem. Soc.* **2018**, *140*, 6336–6342.

[40] S. Pla, M. Niemi, L. Martín-Gomis, F. Fernández-Lázaro, H. Lemmetyinen, N. V. Tkachenko, Á. Sastre-Santos, *Phys. Chem. Chem. Phys.* **2016**, *18*, 3598–3605.

[41] Electronic spectra were corrected for absorptions from the fullerene guest.

[42] Fluorescence emission quenching was also observed upon titration of acyclic receptor *acyclic*-**PDI**[14] with **C_{70}** (Figure S8.4) indicating that dynamic and static quenching contribute to the excited state response of **PBPB**.

[43] Given as an average from four devices, $\mu = 8.02 \pm 0.55 \times 10^{-3}$ cm^2/V•s.

[44] J. C. Barnes, E. J. Dale, A. Prokofjevs, A. Narayanan, I. C. Gibbs-Hall, M. Juríček, C. L. Stern, A. A. Sarjeant, Y. Y. Botros, S. I. Stupp, J. F. Stoddart, *J. Am. Chem. Soc.* **2015**, *137*, 2392–2399.

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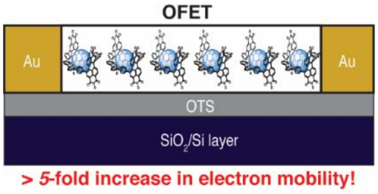

This work reveals a synergy between supramolecular chemistry and molecular electronics. A perylene diimide–bithiophene conjugated macrocycle is shown to act as a potent receptor for fullerenes, resulting in strong electronic communication between host and guest. When incorporated into the active layer of an organic field effect transistor (OFET) device, these supramolecular complexes enhance electron mobility relative to the empty macrocycle.

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