Chemistry–A European Journal
Research Article
doi.org/10.1002/chem.202200254
Chemistry Europe
European Chemical Societies Publishing
www.chemeurj.org

Formation and Photoinduced Electron Transfer in Porphyrin- and Phthalocyanine-Bearing N-Doped Graphene Hybrids Synthesized by Click Chemistry

Luis M. Arellano,[a] Habtom B. Gobeze,[b] Youngwoo Jang,[b] Myriam Barrejón,[c] Concepción Parejo,[d] Julio C. Álvarez,[d] María J. Gómez-Escalonilla,[a] Ángela Sastre-Santos,*[d] Francis D'Souza,*[b] and Fernando Langa*[a]

Abstract: Graphene doped with heteroatoms such as nitrogen, boron, and phosphorous by replacing some of the skeletal carbon atoms is emerging as an important class of two-dimensional materials as it offers the much-needed bandgap for optoelectronic applications and provides better access for chemical functionalization at the heteroatom sites. Covalent grafting of photosensitizers onto such doped graphenes makes them extremely useful for light-induced applications. Herein, we report the covalent functionalization of N-doped graphene (NG) with two well-known electron donor photosensitizers, namely, zinc porphyrin (ZnP) and zinc phthalocyanine (ZnPc), using the simple click chemistry approach. Covalent attachment of ZnP and ZnPc at the N-sites of NG in NG–ZnP and NG–ZnPc hybrids was confirmed by using a range of spectroscopic, thermogravimetric and imaging techniques. Ground- and excited-state interactions in NG–ZnP and NG–ZnPc were monitored by using spectral and electrochemical techniques. Efficient quenching of photosensitizer fluorescence in these hybrids was observed, and the relatively easier oxidations of ZnP and ZnPc supported excited-state charge-separation events. Photoinduced charge separation in NG–ZnP and NG–ZnPc hybrids was confirmed by using the ultrafast pump-probe technique. The measured rate constants were of the order of 10^{10} $s,^{-1}$ thus indicating ultrafast electron transfer phenomena.

Introduction

Graphene, a novel nanomaterial comprising a single sheet of carbon atoms packed in a hexagonal lattice[1–4] has emerged as one of the most actively researched materials for applications in the areas of energy conversion and storage, electrocatalysis, sensors and electronics.[5–11] Controlled chemical doping of heteroatoms such as nitrogen, sulfur, and boron has provided a means of tailoring the properties of graphene, to match those of heteroatom-doped nanotubes, thereby broadening its scope.[12] Among the heteroatom-doped graphenes synthesized, nitrogen-doped graphene (NG), which contains three common bonding configurations within the carbon lattice, namely, quaternary N, pyridinic N and pyrrolic N[13] exhibits properties different from those of pristine graphene including bandgap tuning.

For functionalization purposes, NG offers a significant advantage as it can be conveniently functionalized at the pyrrolic nitrogen sites using established chemical techniques. Recently, we reported a chemical functionalization method that involves the reaction of an alkyl halide at the pyrrolic N.[13] Two donor-acceptor hybrids, namely, NG–C_{60} and NG-perylene diimide (PDI), in which electron-deficient C_{60}[14] and PDI[15] serve as electron acceptors, were successfully synthesized using this approach. Subsequently, photoinduced charge separation leading to $NG^{\bullet+}$–$C_{60}^{\bullet-}$ and $NG^{\bullet+}$–$PDI^{\bullet-}$ states was confirmed using time-resolved pump-probe techniques. In other words, NG is acting as an electron donor in these systems.[14,15] However, a literature search showed that the ability of NG to act as an electron acceptor under light illumination conditions has yet to be established. This becomes especially important for the application of NG in light-energy and light-to-fuel conversion and other catalytic applications.[16] With this in mind, in the

[a] Dr. L. M. Arellano, Dr. M. J. Gómez-Escalonilla, Prof. F. Langa
Universidad de Castilla-La Mancha
Instituto de Nanociencia, Nanotecnología y Materiales Moleculares (INAMOL)
Avda. Carlos III, s/n, 45071-Toledo (Spain)
E-mail: Fernando.Langa@uclm.es

[b] Dr. H. B. Gobeze, Y. Jang, Prof. F. D'Souza
Department of Chemistry and Materials Science and Engineering
University of North Texas, Denton, TX 76203-5017 (USA)
E-mail: francis.dsouza@unt.edu

[c] Dr. M. Barrejón
Neural Repair and Biomaterials Laboratory
Hospital Nacional de Parapléjicos (SESCAM)
Finca la Peraleda s/n, 45071 Toledo (Spain)

[d] Dr. C. Parejo, Dr. J. C. Álvarez, Prof. Á. Sastre-Santos
Área de Química Orgánica, Instituto de Bioingeniería
Universidad Miguel Hernández
Avda. de la Universidad, s/n, Elche 03202 (Spain)
E-mail: asastre@umh.es

Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202200254

was run under argon atmosphere. Experiments were done in a one-compartment cell equipped with a platinum working microelectrode (Ø = 2 mm) and a platinum wire counter electrode. A scan rate of 0.1 $V s^{-1}$ was used. An $Ag/AgNO_3$ electrode was used as reference and checked against the ferrocene/ferrocenium couple (Fc/Fc^+) before and after each experiment.

Femtosecond transient absorption spectroscopy experiments were carried out using an ultrafast femtosecond laser source (Libra) by Coherent incorporating diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with femtosecond harmonics generator both provided by Ultrafast Systems LLC was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into a TOPAS-Prime-OPA system with 290–2600 nm tuning range from Altos Photonics Inc., (Bozeman, MT), while the rest of the output was used for generation of white light continuum. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K.

Acknowledgments

This work was financially supported by MICINN of Spain (PID2019-105049RB–I00 to F.L., CTQ2017-87102-R and PID2020-117855RB–I00 to ASS) and the Junta de Comunidades de Castilla – La Mancha together with European FEDER funds (SBPLY/17/180501/000254) and by the US National Science Foundation (1401188 and 2000988 to F.D.). M.A. thanks MINECO for a doctoral FPI grant. M.B.A. is grateful to the Instituto de Salud Carlos III for a Sara Borrell Fellowship (CD18/00145).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Keywords: click chemistry · N-doped graphene · photoinduced electron-transfer · zinc phthalocyanines · zinc porphyrins

[1] S. Nasir, M. Z. Hussein, Z. Zainal, N. A. Yusof, *Materials* **2018**, *11*, 295–319.
[2] V. Georgakilas, J. A. Perman, J. Tucek, R. Zboril, *Chem. Rev.* **2015**, *115*, 4744–4822.
[3] Z. Li, Z. Liu, H. Sun, C. Gao, *Chem. Rev.* **2015**, *115*, 7046–7117.
[4] G. Bottari, M. Ángeles Herranz, L. Wibmer, M. Volland, L. Rodríguez-Pérez, D. M. Guldi, A. Hirsch, N. Martín, F. D'Souza, T. Torres, *Chem. Soc. Rev.* **2017**, *46*, 4464–4500.
[5] O. Ito, *Chem. Rec.* **2017**, *17*, 326–362.
[6] F. D'Souza, O. Ito, *Chem. Soc. Rev.* **2012**, *41*, 86–96.
[7] V. Sgobba, D. M. Guldi, *Chem. Soc. Rev.* **2009**, *38*, 165–184.
[8] G. Bottari, G. de La Torre, D. M. Guldi, T. Torres, *Chem. Rev.* **2010**, *110*, 6768–6816.
[9] D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks, M. C. Hersam, *Chem. Soc. Rev.* **2013**, *42*, 2824–2860.
[10] T. Umeyama, H. Imahori, *J. Phys. Chem. C* **2013**, *117*, 3195–3209.
[11] T. Umeyama, H. Imahori, *Nanoscale Horiz.* **2018**, *3*, 352–366.
[12] H. Wang, T. Maiyalagan, X. Wang, *ACS Catal.* **2012**, *2*, 781–794.
[13] M. Barrejón, A. Primo, M. J. Gómez-Escalonilla, J. L. García-Fierro, H. García, F. Langa, *Chem. Commun.* **2015**, *51*, 16916–16919.
[14] M. Barrejón, L. M. Arellano, H. B. Gobeze, M. J. Gómez-Escalonilla, J. L. García-Fierro, F. D'Souza, F. Langa, *Chem. Sci.* **2018**, *9*, 8221–8227.
[15] H. B. Gobeze, L. M. Arellano, A. M. Gutiérrez-Vílchez, M. J. Gómez-Escalonilla, Á. Sastre-Santos, F. Fernández-Lázaro, F. Langa, F. D'Souza, *Nanoscale Adv.* **2019**, *1*, 4009–4015.
[16] C. Hu, D. Liu, Y. Xiao, L. Dai, *Prog. Nat. Sci.* **2018**, *28*, 121–132.
[17] J.-H. Chou, M. E. Kosal, H. S. Nalwa, N. A. Rakow, K. S. Suslick in, *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard) Academic Press, New York, **2000**, p. 43.
[18] G. de La Torre, C. G. Claessens, T. Torres, *Chem. Commun.* **2007**, 2000–2015.
[19] J. Mack, N. Kobayashi, *Chem. Rev.* **2011**, *111*, 281–321.
[20] L. M. Arellano, M. Barrejón, H. B. Gobeze, M. J. Gómez-Escalonilla, J. L. García-Fierro, F. D'Souza, F. Langa, *Nanoscale* **2017**, *9*, 7551–7558.
[21] A. Aljarilla, J. N. Clifford, L. Pellejà, A. Moncho, S. Arrechea, P. D. la Cruz, F. Langa, E. Palomares, *J. Mater. Chem. A* **2013**, *1*, 13640–13647.
[22] M. Barrejón, M. Vizuete, M. J. Gómez-Escalonilla, J. L. García-Fierro, I. Berlanga, F. Zamora, G. Abellán, P. Atienzar, J. F. Nierengarten, H. García, F. Langa, *Chem. Commun.* **2014**, *50*, 9053–9055.
[23] M. Vizuete, M. J. Gómez-Escalonilla, J. L. García-Fierro, M. Yudasaka, S. Iijima, M. Vartanian, J. Iehl, J. F. Nierengarten, F. Langa, *Chem. Commun.* **2011**, *47*, 12771–12773.
[24] M. Vizuete, M. J. Gómez-Escalonilla, J. L. García-Fierro, A. S. D. Sandanayaka, T. Hasobe, M. Yudasaka, S. Iijima, O. Ito, F. Langa, *Chem. Eur. J.* **2010**, *16*, 10752–10763.
[25] J. Mateos-Gil, L. Rodríguez-Pérez, M. Moreno Oliva, G. Katsukis, C. Romero-Nieto, M. Á. Herranz, D. M. Guldi, N. Martín, *Nanoscale* **2015**, *7*, 1193–1200.
[26] L. Martín-Gomis, C. Parejo, J. C. Álvarez, F. Fernández-Lázaro, Á. Sastre-Santos, *Inorg. Chim. Acta* **2017**, *468*, 327–333.
[27] B. J. Campo, J. Duchateau, C. R. Ganivet, B. Ballesteros, J. Gilot, M. M. Wienk, W. D. Oosterbaan, L. Lutsen, T. J. Cleij, G. de La Torre, R. A. J. Janssen, D. Vanderzande, T. Torres, *Dalton Trans.* **2011**, *40*, 3979–3988.
[28] L. Rodríguez-Pérez, J. Ramos-Soriano, A. Pérez-Sánchez, B. M. Illescas, A. Muñoz, J. Luczkowiak, F. Lasala, J. Rojo, R. Delgado, N. Martín, *J. Am. Chem. Soc.* **2018**, *140*, 9891–9898.
[29] H. J. Shin, M. K. Soo, S. M. Yoon, A. Benayad, K. K. Ki, J. K. Sung, K. P. Hyun, J. Y. Choi, H. L. Young, *J. Am. Chem. Soc.* **2008**, *130*, 2062–2066.
[30] L. M. Arellano, H. B. Gobeze, M. J. Gómez-Escalonilla, J. L. García-Fierro, F. D'Souza, F. Langa, *Nanoscale* **2020**, *12*, 9890–9898.
[31] L. M. Arellano, L. Martín-Gomis, H. B. Gobeze, D. Molina, C. Hermosa, M. J. Gómez-Escalonilla, J. L. García-Fierro, Á. Sastre-Santos, F. D'Souza, F. Langa, *Nanoscale* **2018**, *10*, 5205–5213.
[32] J. P. Collman, N. K. Devaraj, T. P. A. Eberspacher, C. E. D. Chidsey, *Langmuir* **2006**, *22*, 2457–2464.
[33] C. B. Kc, G. N. Lim, F. D'Souza, *Nanoscale* **2015**, *7*, 6813–6826.
[34] F. D'Souza, S. Gadde, D. M. Shafiqul Islam, C. A. Wijesinghe, A. L. Schumacher, M. E. Zandler, Y. Araki, O. Ito, *J. Phys. Chem. A* **2007**, *111*, 8552–8560.
[35] S. K. Das, A. Mahler, A. K. Wilson, F. D'Souza, *ChemPhysChem* **2014**, *15*, 2462–2472.
[36] M. Barrejón, L. M. Arellano, F. D'Souza, F. Langa, *Nanoscale* **2019**, *11*, 14978–14992.
[37] M. Barrejón, H. B. Gobeze, M. J. Gómez-Escalonilla, J. L. García-Fierro, M. Zhang, M. Yudasaka, S. Iijima, F. D'Souza, F. Langa, *Nanoscale* **2016**, *8*, 14716–14724.

Manuscript received: January 26, 2022
Accepted manuscript online: March 7, 2022
Version of record online: March 28, 2022