

Azafullerene-based donor-acceptor dyads

Georgios Rotas and Nikos Tagmatarchis*

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation

48 Vassileos Contantinou Avenue, Athens 11635, Greece

E-mail: tagmatar@eie.gr

Dedicated to Prof. Michael Orfanopoulos on the occasion of his 67th birthday anniversary

DOI: <http://dx.doi.org/10.3998/ark.5550190.p008.987>

Abstract

A large amount of research effort focuses on the synthesis and properties of donor-acceptor systems for energy conversion schemes. In this context, fullerenes are novel energy/electron acceptors. Azafullerene C₅₉N, which formally arises from the replacement of one carbon of C₆₀ by a nitrogen atom, is derivatized mainly by electrophilic aromatic substitution and Mannich type reactions, thus offering immediate access to diverse dyads. Herein, the aforementioned functionalization methods will be highlighted, especially with regards to the preparation of C₅₉N-based donor-acceptor dyads. Particular attention will be given to the energy and charge transfer properties of the C₅₉N-based dyads incorporating ferrocene, polycyclic aromatic hydrocarbons, porphyrins, phthalocyanine, corrole and gold nanoparticles.

Keywords: Azafullerene; functionalization; donor-acceptor dyads; photophysics; electrochemistry

Table of Contents

1. Introduction
2. Chemistry of azafullerenes
3. Donor-acceptor dyads
4. Conclusions
5. References

1. Introduction

The first heterofullerene synthesized via the replacement of a carbon atom of an all-carbon fullerene by different species was azafullerene.¹ The latter replacement effectively led to n-doping of the material, and importantly affected the bonding of the carbon sphere of C₆₀ giving rise to the dimer (C₅₉N)₂ with a σ bond connecting the two carbons adjacent to nitrogen. n-Doping alters the electronic and optical properties, particularly the charge distribution, electronic structure and energy HOMO-LUMO gap of azafullerenes, as demonstrated by theoretical calculations.² Therefore, azafullerenes are considered suitable materials to be incorporated in advanced technological applications, especially in energy conversion manifolds. In this regard, their development relies on the preparation of diverse hybrids, particularly those in donor-acceptor dyads, and on the evaluation of their properties. In addition, azafullerene-based materials were recently used as acceptors in bulk heterojunction solar cells (BHJSCs) with promising results: a pentaaryl functionalized C₅₉N, possessing a raised LUMO as compared to the “benchmark” PC₆₁BM, matched better to the P3HT donor moiety,³ while a bis-functionalized C₅₉N, carrying a thiophene and a fused phenylcyclohexyl moiety was also incorporated as an acceptor in BHJSCs, though the performance of the cells have yet to be optimized.⁴

The preparation of bisazafullerene (C₅₉N)₂ from the parent fullerene C₆₀ is based on a well described method,¹ and methods for the chemical modification of C₅₉N have already been comprehensively reviewed.⁵⁻⁷ As such, in the current review only some essential aspects will be briefly outlined. The review is organized in three main sections: the first deals with the chemistry of azafullerenes; next, the synthesis of C₅₉N-based donor-acceptor dyads and their photophysical evaluation towards charge-transfer processes; and finally, a summary and some concluding remarks are given in the last section of the review.

2. Chemistry of azafullerene

Azafullerene in its dimer form (C₅₉N)₂ was first synthesized from the *N*-MEM-ketolactam **1** (prepared in two steps from C₆₀)⁸ in refluxing *o*-dichlorobenzene (ODCB) under inert atmosphere, in the presence of *p*-toluenesulfonic acid (*p*-TsOH) (Scheme 1).¹ Owing to the presence of the trivalent nitrogen atom, azafullerene is isolated in its dimeric form (C₅₉N)₂ **2**. Later, an optimization of the reaction conditions led to improved purities and reproducibly higher yield,⁹ allowing easier access to (C₅₉N)₂, thus boosting the investigation of its chemistry towards the production of diverse C₅₉N derivatives.

All-carbon fullerenes, whose reaction centers (namely the [6,6] bonds) are in general uniformly dispersed around the sphere, afford in principle, apart from the desirable mono-adduct, also multi-adducts upon derivatization.¹⁰ In these cases, cycloaddition strategies are the usually employed towards derivatization. On the other hand, in azafullerenes the presence of an *sp*³ carbon next to the nitrogen atom is a reactive center different from the aforementioned described

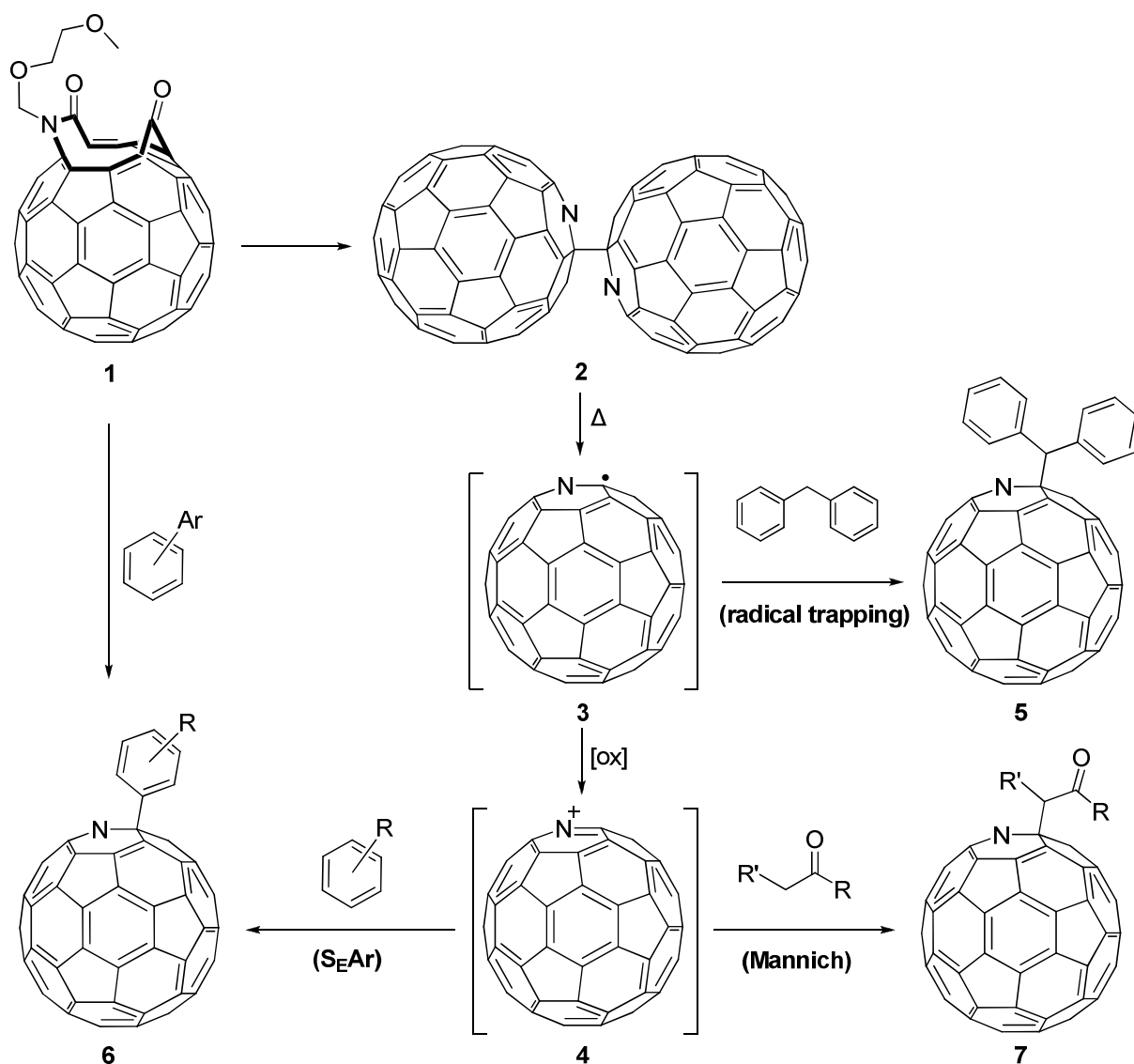
[6,6] bonds. Therefore, exploitation of the sp^3 carbon atom in $C_{59}N$ results in different chemistry from that of all-carbon fullerenes, while at the same time, affords exclusively mono-adducts; multi-adducts, if desired, can subsequently be formed with cycloaddition reactions on the mono-adducts.¹¹

Chemical derivatization of $C_{59}N$ is based on the fact that upon heating, the intra-dimer bond of $(C_{59}N)_2$ dissociates homolytically towards the azafullerene radical **3**. The latter radical can be either trapped by other radicals to form azafullerene derivatives,¹²⁻¹⁴ such as **5**, or in the presence of an oxidant, afford the azafullerenyl cation **4**, which can then react with nucleophiles. The latter method is by far the most widely used for the functionalization of $C_{59}N$ ¹⁵ and has been employed in the two main reactions for the preparation of $C_{59}N$ derivatives, namely, the electrophilic aromatic substitution (S_EAr)¹⁶ and the Mannich type reaction;¹⁷ photoinduced electron transfer reactions of **4** have also been reported.^{18,19} In the first, azafullerene reacts with activated aryl compounds, resulting in derivatives **6**, where the $C_{59}N$ sphere is directly attached to an aromatic ring. In this reaction, the *N*-MEM-ketolactam has also been employed as starting material instead of $(C_{59}N)_2$, yielding the same arylated azafullerene, albeit in lower yield. In the Mannich reaction, enolizable carbonyl compounds such as ketones, malonates, or aldehydes are the functionalization agents, affording the corresponding Mannich bases **7**. In both cases, moderate to high yields of $C_{59}N$ derivatives are generally obtained, while the reaction conditions involve in general heating an ODCB solution of $(C_{59}N)_2$ at 150 °C in the presence of excess *p*-TsOH and the appropriate reactant (aryl or carbonyl derivative), with a constant stream of air for upto several hours.

3. Donor-acceptor dyads

The photophysical properties of azafullerene derivatives such as **6** and **7**, present both similarities and differences compared to fullerene monoadducts.^{7,20,21} The electronic absorption spectra of azafullerene derivatives are usually similar to that of $(C_{59}N)_2$ and mainly consist of a set of four characteristic bands. A strong ($\epsilon \approx 6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) one in the UV region at 320 nm, one of medium intensity at 445 nm, and two weak bands at 720 and 805 nm. The latter is related to the S^0-S^1 transition, and its mirror image is reflected in the fluorescence spectra of $C_{59}N$ derivatives, showing a weak ($\Phi_F \approx 2.8 \times 10^{-4}$ in toluene) emission band at 815–825 nm. This is a significant difference with C_{60} mono-adducts, which show a S^0-S^1 absorption band at around 690 nm and emission ($\Phi_F \approx 5 \times 10^{-4}$ in toluene) at ~ 710 nm. Thus, the azafullerene singlet excited state (~ 1.52 eV) lies about 0.27 eV lower in energy than that of functionalized C_{60} , rendering energy transfer to $C_{59}N$ easier. In fact, the $C_{59}N$ fluorescence lifetime of ~ 0.8 ns is almost half of those of C_{60} derivatives, in accordance to the steady state emission behavior. Regarding the $C_{59}N$ ¹⁸ deactivation, intersystem crossing (ISC) to the triplet manifold occurs, as in the case of C_{60} derivatives, albeit in lower yield ($\Phi_T \approx 0.3$ as compared to ~ 1 for C_{60}). The latter reflects the ability of azafullerene to act as photosensitizer for the formation of singlet oxygen upon

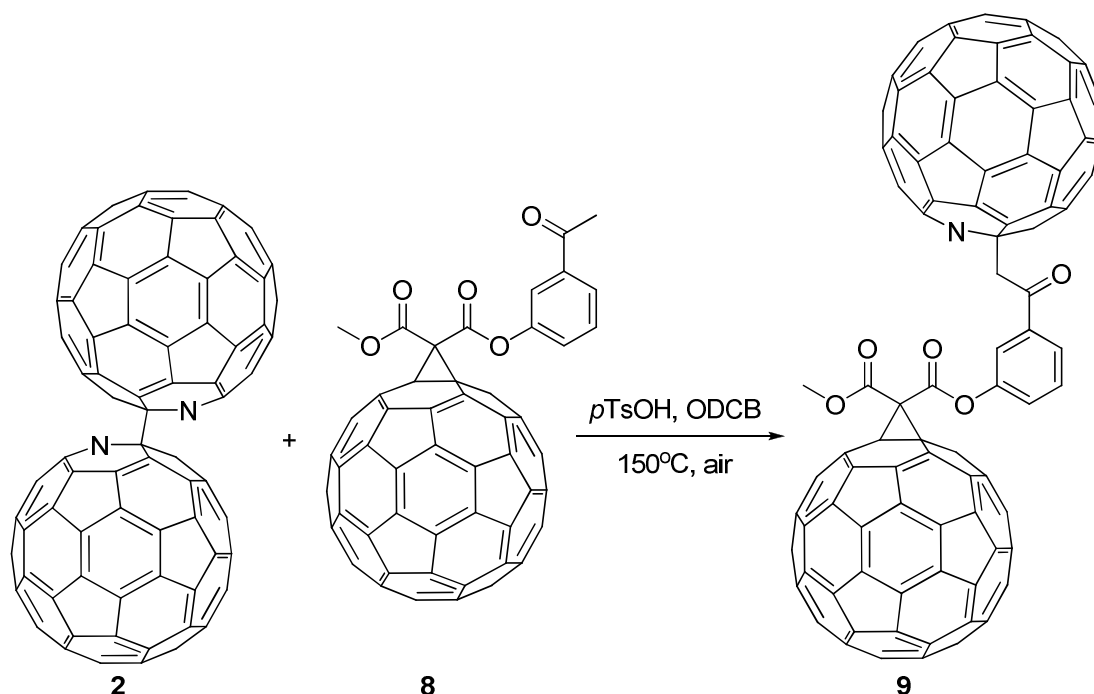
irradiation.²²⁻²⁴ Finally, the higher electronegativity of the nitrogen atom is reflected in the electrochemistry of azafullerene derivatives, which usually exhibit three quasi-reversible reduction waves. The first reduction is usually found at more positive potentials than that of C₆₀ derivatives, that is, easier to reduce, thus rendering C₅₉N a potential better electron acceptor in donor acceptor systems.



Scheme 1. Main routes for the functionalization of azafullerene, either directly from (C₅₉N)₂ **2** or via the precursor *N*-MEM-ketolactam **1**.

Since C₅₉N is by default compared to C₆₀ as acceptor, it would be useful to begin with the properties of an interesting C₅₉N-C₆₀ dyad. By employing the Mannich reaction of (C₅₉N)₂ with an equimolar amount of the acetyl functionalized C₆₀ derivative **8**, dyad **9** (Scheme 2) was

isolated in 27% yield.²⁵ Concerning its photophysical properties, the absorption spectrum of **9** appears as a superimposition of those of a fullerene monoadduct and (C₅₉N)₂. Semiempirical calculations showed that the LUMO of the dyad is located at the C₅₉N core, a fact that is supported by electrochemical measurements, and that the reduction of C₅₉N is easier than that of C₆₀ by about 0.2 V (in THF). Regarding the excited state properties, the emission spectrum of **9** shows both C₆₀ and C₅₉N emission peaks at 705 and 825 nm, respectively, the former quenched and the latter enhanced relatively to appropriate reference materials. In accordance with this observation, complementary time resolved fluorescence and transient absorption measurements revealed that irradiation of **9** at first results in excitation of both C₆₀ and C₅₉N cores to their singlet excited states. Then, deactivation of C₆₀^{1S} almost totally occurs through energy transfer to C₅₉N^{1S}, which in turn decays through ISC to the azafullerene triplet excited state.



Scheme 2. Synthesis of the C₆₀-C₅₉N dyad **9**.

The first C₅₉N based donor-acceptor dyad, where a ferrocene moiety is directly attached on the azafullerene sphere, compound **10** (Figure 1), was also the first fullerene based dyad where the donor is directly connected to the fullerene via a single bond.²⁶ The synthesis was accomplished using the S_EAr strategy but in the absence of air flow and *p*-TsOH, since the role of oxidant was played by ferrocene. With the aid of 25 equivalents of ferrocenium hexafluorophosphate the product was formed in “acceptable yield”. Extensive electrochemical studies of the dyad, together with those of reference C₅₉N and ferrocene materials, revealed a significant positive shift of the Fc oxidation signal (by 183 mV relative to that of the parent ferrocene), together with a minor negative shift of the three C₅₉N-originated reduction potentials.

In addition, the absorption spectrum of the dyad appeared different from a simple superimposition of the component chromophores' spectra. In combination, the above observations suggest significant electronic interactions in the ground state. Concerning the excited state, the characteristic emission of $C_{59}N$ at around 820 nm was significantly quenched in the dyad, revealing a fast deactivation of the azafullerene singlet excited state. Furthermore, transient absorption spectroscopy showed no evidence of the ferrocene triplet excited state (thus precluding a singlet-triplet energy transfer). In contrast, the existence of an absorption attributed to one electron oxidation of ferrocene suggested the intramolecular charge transfer as the source of the observed azafullerene singlet excited state deactivation. Charge-separated (CS) state lifetimes of 0.4 ns (in benzonitrile) and 0.27 ns (in toluene) were calculated.

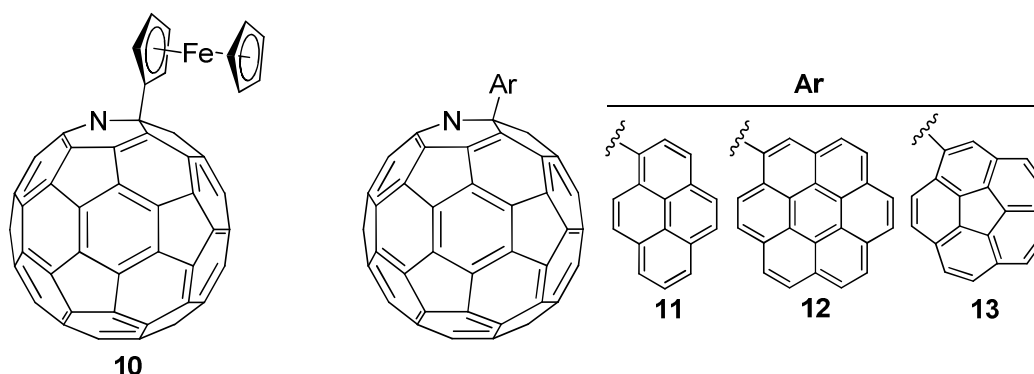


Figure 1. $C_{59}N$ -based dyads prepared with the S_EAr strategy.

In another work, dyads **11-13** were synthesized,²⁷ employing the S_EAr strategy (Figure 1). Here, the polycyclic aromatic hydrocarbons (PAHs) pyrene, coronene and corannulene were connected through a single bond with the azafullerene. Briefly, 1 equivalent of the PAH was used in the reaction, affording the products **11-13** in yields 18, 17 and 9%, respectively. The electronic interactions of the dyads were monitored with steady state emission spectroscopy, revealing an almost complete quenching of the PAH emission in the visible region. On the other hand, the emission of the azafullerene remains intact, despite the nearly exclusive excitation of the PAH moiety. In addition, the excitation spectra monitoring the emission of the $C_{59}N$ moiety, showed the characteristic absorption patterns of the PAHs. In time-resolved fluorescence, the lifetime of the $C_{59}N$ moiety appears the same as that of the reference $C_{59}N$ material (~ 1 ns). In complementary transient absorption measurements, the spectra recorded immediately after the 18 ps laser pulse showed only a broad absorption at 940 nm (attributed to $C_{59}N^{1S}$) and not to that of the PAH^{1S} expected in the visible region. Thus, all the evidence pointed to the PAHs ultra-fast singlet excited state deactivation via energy transfer to $C_{59}N$.

In the aforementioned $C_{59}N$ -based dyads, the π electron cloud of the donor lies perpendicular to the azafullerene sphere owing to the rigid structure of the molecule, possibly hampering intramolecular electronic communication. Thus, in a complementary study, a series of aromatic

systems were used as donors, this time employing the Mannich synthetic approach with acetyl-substituted donors as reactants. In this way, a relatively more flexible linker connects the two chromophores, possibly allowing for a better conformation for electronic communication to occur. Thus, dyads **14-18** were synthesized (Figure 2) in 14–55% yields, using 7.5–30 equivalents of the appropriate acetyl-substituted compound.²⁸ A study of the ^1H and ^{13}C NMR spectra of the dyads, showed evidence that support both an anti-periplanar (extended, no π - π interaction) and a folded (efficient π - π interaction) conformation, leading to the conclusion that a back-folding tendency, attributed to π - π stacking, is fighting the sterically favored extended conformation, ultimately resulting in rather free rotation. Considering the photophysical properties, absorption spectra of the dyads appear as superimpositions of the component chromophores, thus precluding ground state interactions. Monitoring the excited state features, the near-visible region centered donor emission (340–400 nm) of the dyads **14-18** was found quenched by a factor of 3–7 relative to that of the acetyl-functionalized aromatics (and a factor of as large as 1100 relative to the parent aromatics). Regarding the azafullerene emission (~ 825 nm), the same observations as in the case of dyads **11-13** mentioned above, irrespectively of the solvent polarity, led to the conclusion of an efficient intramolecular energy transfer. This observation was verified with transient absorption measurements. The singlet excited state of the fluorophore appears at low time scales with short lifetimes (~ 100 ps), while later, the $\text{C}_{59}\text{N}^{18}$ appears (~ 940 nm) as a meta-stable condition which decays via ISC to the triplet excited state.

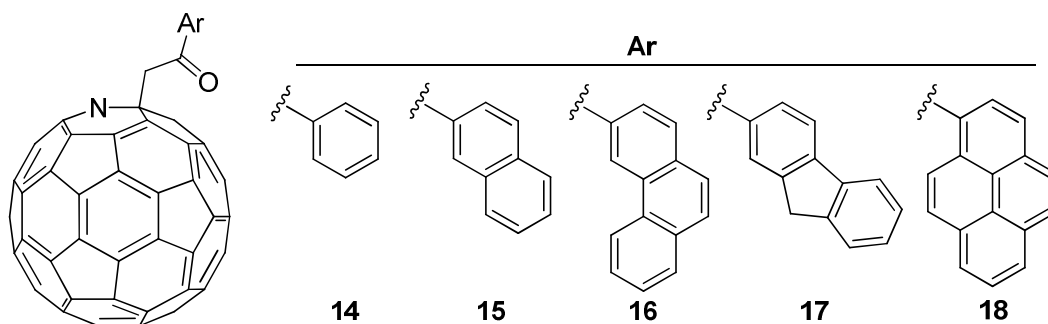


Figure 2. (Poly)aromatic hydrocarbon C_{59}N -based derivatives prepared via the Mannich strategy.

Porphyrins are widely known as excellent electron donors and in this context, numerous porphyrin-fullerene donor-acceptor systems have been synthesized and their properties towards efficient charge separation have been investigated. The first work on covalently linked porphyrin-azafullerene systems involved the synthesis and photophysical study of dyads **19** and **20** (Figure 3).²⁹ The syntheses were accomplished with the Mannich strategy, employing an equimolar amount of a malonate or an acetyl functionalized tetraphenyl porphyrin (TPP) in moderate yields. Concerning their photophysical properties, the strong porphyrin emission appears quenched by a factor of around 50 in both dyads. Interestingly, while the observed

quenching rate of **20** increases with the polarity of the solvent employed (attributed to through bond electron transfer), that of **19** remains intact (attributed to solvent-assisted through space electron transfer, owing to greater configurational freedom). Transient absorption measurements showed $\text{TPP}^{1\text{S}}$ lifetimes of ~ 0.35 ns for **19** (independent of the solvent) while for **20**, $\text{TPP}^{1\text{S}}$ lifetimes of 0.19 and 0.08 ns were observed in THF and more polar benzonitrile, respectively. The kinetics of the charge separated states, as monitored from the decays of TPP^{*+} (600-700 nm) and $\text{C}_{59}\text{N}^{\bullet-}$ (1010 nm), revealed shortening of radical ion pair lifetimes on increasing solvent polarity (445 and 362 ns for **19**, and 260 and 155 ns for **20**, in THF and benzonitrile, respectively). This observation is rationalized in terms of the Marcus theory of electron transfer, where the charge-separation rate decreases on increasing the driving force for systems that lie in the inverted region.

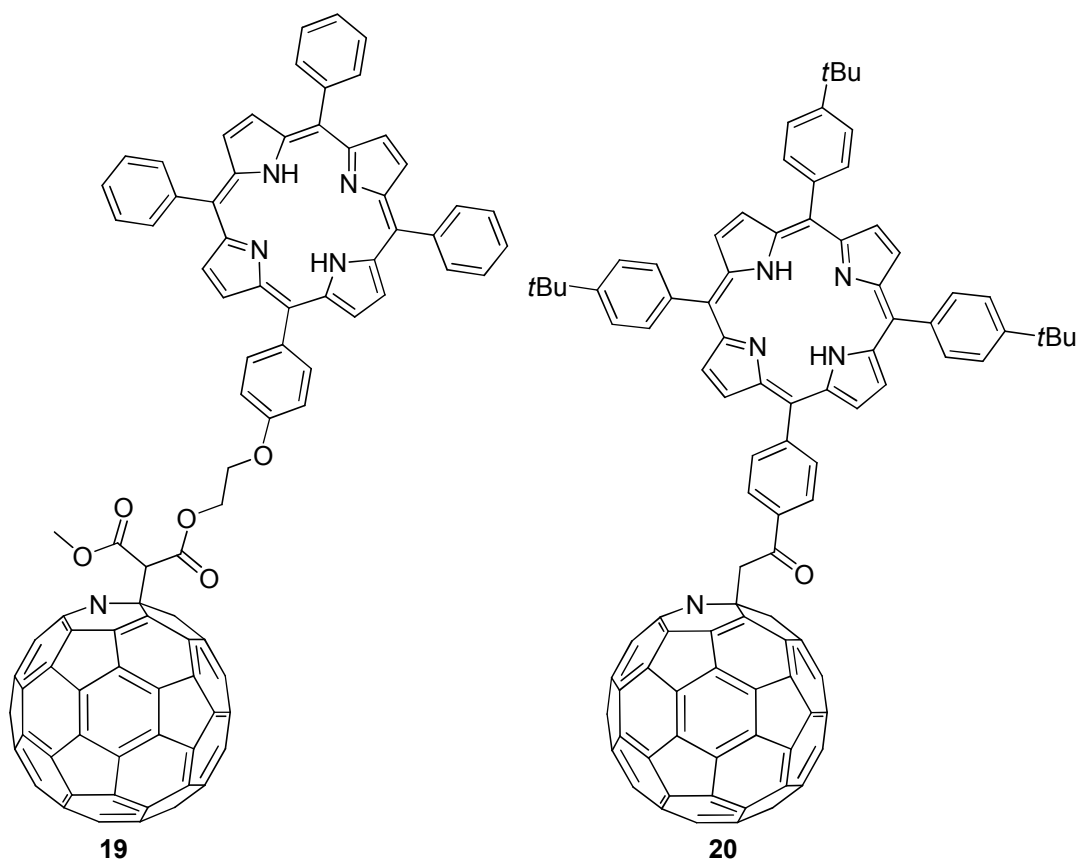


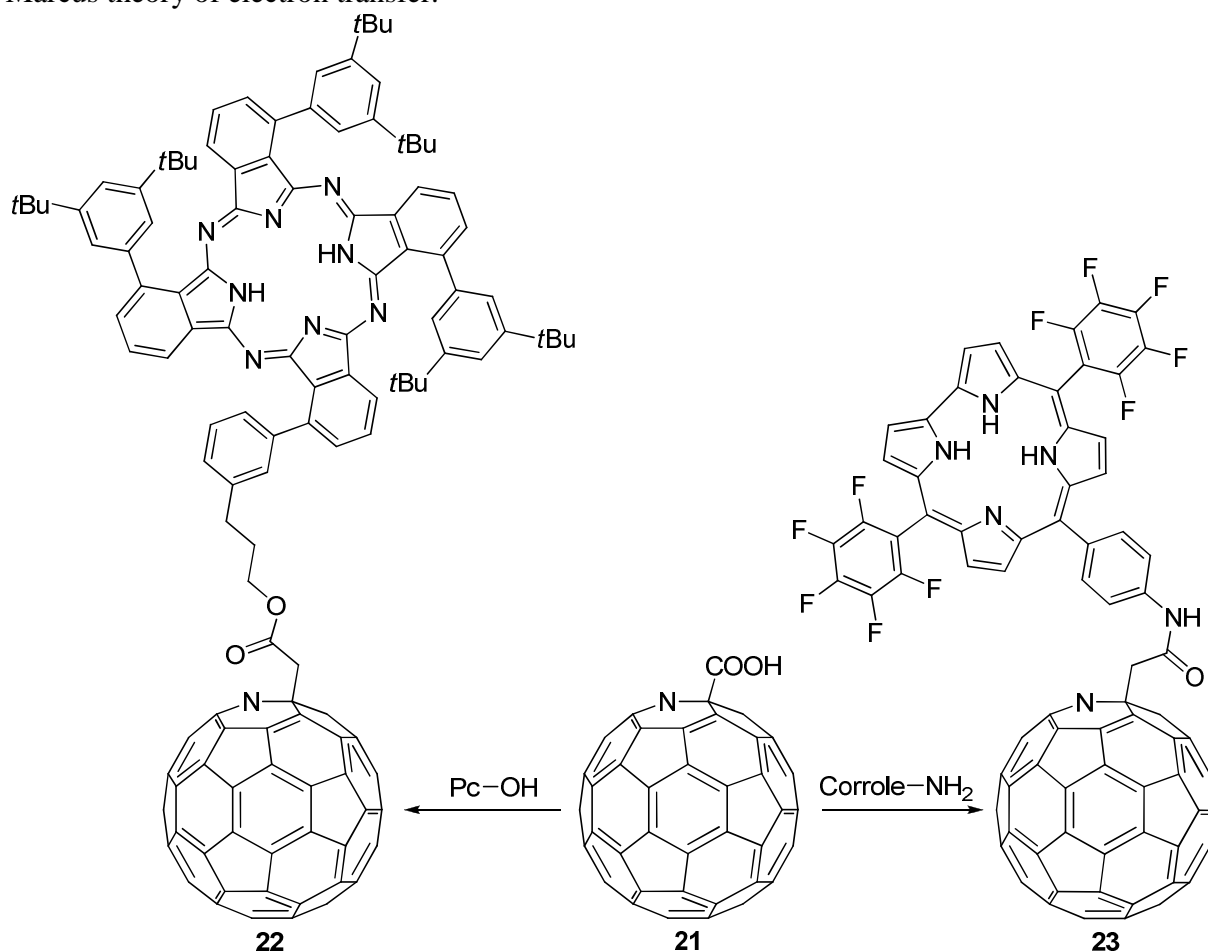
Figure 3. Covalently attached porphyrins to azafullerene; C₅₉N–porphyrin dyads **19** and **20**.

A different synthetic route towards C₅₉N-based donor-acceptor dyads involved at first the synthesis of an azafullerene derivative bearing a functional group, which subsequently reacts with an appropriately functionalized donor. Thus, the carboxylic acid functionalized C₅₉N **21** (Scheme 3), prepared in 55% yield by the Mannich reaction of (C₅₉N)₂ with 50 equivalents of

t-butyl malonate)³⁰ enabled the use of hydroxyl or amino-functionalized donor derivatives for the preparation of dyads, while at the same time, the relatively harsh conditions of the C₅₉N functionalization (150 °C, *p*-TsOH, air) were replaced by the smooth ones of a condensation reaction. In this context, an equimolar amount of **21** and a hydroxyl functionalized phthalocyanine (H₂Pc) were condensed with the aid of EDCI/HOBt towards dyad **22** (34% yield). While weak ground state interactions between the two chromophores were observed, the 128-fold quenching of the H₂Pc emission revealed strong excited state interactions. Monitoring the azafullerene emission, in non-polar toluene was found enhanced (suggesting energy transfer from H₂Pc) relative to the reference C₅₉N, while in polar benzonitrile was found quenched, thus suggesting electron transfer. Interestingly, electrochemical measurements revealed a somewhat lower charge separated state energy than that of C₅₉N^{1S}-H₂Pc, suggesting a possible charge transfer from azafullerene singlet excited state (apart from H₂Pc^{1S}) in polar solvents. Complementary transient absorption measurements revealed quite different deactivation behavior of the dyad after excitation in toluene and in benzonitrile. In toluene, absence of charge separated state formation was verified and a sequence of energy transfer reactions and transitions were found to occur towards the H₂Pc triplet excited state (C₅₉N-H₂Pc^{1S} → C₅₉N^{1S}-H₂Pc → C₅₉N^{1T}-H₂Pc → C₅₉N-H₂Pc^{1T}). A completely different deactivation pathway was observed in benzonitrile, where the formation of the charge separated state dominates in deactivation, but the main pathway is again a multi-step one, including energy transfer to C₅₉N prior to the electron transfer (C₅₉N-H₂Pc^{1S} → C₅₉N^{1S}-H₂Pc → C₅₉N^{•-}-H₂Pc^{•+}). Also, the photophysical properties of C₅₉N-H₂Pc **22** were compared to those of a previously reported C₆₀-H₂Pc dyad.³¹ The lower energy of C₅₉N^{1S} compared to that of C₆₀^{1S} explained the ease of energy transfer in **22** even in benzonitrile, since C₅₉N^{1S}-H₂Pc lies energetically lower than C₅₉N-H₂Pc^{1S}, while the opposite was observed in the C₆₀-H₂Pc dyad. Thus, although the charge separated states' lifetimes of **22** and C₆₀-H₂Pc in benzonitrile were comparable (190 and 320 ps, respectively), the electron transfer process is much slower (15 ps) in **22** than in C₆₀-H₂Pc (2 ps), a fact attributed to the extra step of energy transfer.

Carboxylic acid functionalized C₅₉N **21** was also used for the synthesis of the C₅₉N-corrole dyad **23**³² (Scheme 3), through a condensation reaction of an equimolar amount of **21** and an amino-functionalized corrole in 8% yield. The strong emission of the corrole at around 660 nm was quenched in the dyad by a factor of 20–116 depending of the solvent employed, while a similar trend was observed in emission lifetime experiments. Interestingly, transient absorption measurements of dyad **23** showed the electron transfer to be the route for the observed deactivation of corrole singlet excited state, in polar and non-polar solvents alike. Monitoring the process in *o*-xylene, toluene, anisole, 2-methyl-THF and benzonitrile, a predictable gradual decrease of the corrole singlet excited state lifetime was observed on increasing solvent polarity (from 166 ps to 16 ps, as monitored by the corrole^{1S} 1240 nm transient absorption) and in parallel, a gradual decrease of the radical ion pair C₅₉N^{•-}-corrole^{•+} lifetime (from 1 ns to 65 ps, monitoring the C₅₉N^{•-} absorption at 1040 nm). The latter trend of diminishing CS lifetime upon

increasing solvent polarity was rationalized, as in the cases of **19** and **20** (see above), using the Marcus theory of electron transfer.



Scheme 3. Use of carboxylic acid C₅₉N-based derivative **21** in the preparation of donor-acceptor systems.

In a rather different approach to those described above, the properties of a supramolecular assembly of an azafullerene derivative with a zinc porphyrin (ZnTPP) were studied.³³ A pyridine functionalized C₅₉N (prepared in 78% yield by the Mannich approach using 200 equivalents of 4-acetylpyridine) together with an equimolar amount of ZnTPP were dissolved in deuterated ODCB to study by NMR spectroscopy the formation of the complex **24** (Figure 4). The spectrum showed no evidence of free ZnTPP, as well as a remarkable upfield shift of the α -pyridine protons' signal by 5 ppm, verifying an almost complete complexation of the two chromophores. Furthermore, ZnTPP absorption spectrum showed a red shift (2-4 nm) of both *Q* and Soret bands on adding C₅₉N-pyridine. Steady state emission of ZnTPP also showed a gradual quenching (up to 25 fold), while time resolved measurements turned emission lifetime from a monoexponential of 2 ns for free ZnTPP, to a biexponential of 1.9 and 0.12-0.15 ns, with

increasing contribution of the short-lived component, on increasing C₅₉N-pyridine concentration in non-coordinating solvents (toluene, ODCB). The original emission properties of ZnTPP were restored on addition of THF or pyridine, suggesting the dissolution of the complex **24** in the presence of coordinating compounds. Correlating the emission quenching with the C₅₉N-pyridine concentration, association constants for the formation of **24** of 9500 and 11700 M⁻¹ for toluene and ODCB, respectively were derived. Concerning the deactivation mechanism of ZnTPP^{1S}, an increase of the C₅₉N emission together with the ZnTPP emission quenching in toluene indicated energy transfer (ZnTPP^{1S}-C₅₉N → ZnTPP-C₅₉N^{1S}), a fact that was reinforced by transient absorption measurements, where ZnTPP-C₅₉N^{1S} was found to further decay to ZnTPP-C₅₉N^{1T}. This observation was set in contrast to the mechanism of a similar C₆₀-ZnTPP supramolecular dyad,³⁴ where electron transfer dominates even in toluene. On the other hand, charge transfer was the deactivation path in the more polar ODCB. Here, the formation of the charge-separated state is energetically more favorable and its formation was verified by the presence of the C₅₉N^{•-} and ZnTPP^{•+} transient absorption peaks, yielding a radical ion pair lifetime of 145 ns.

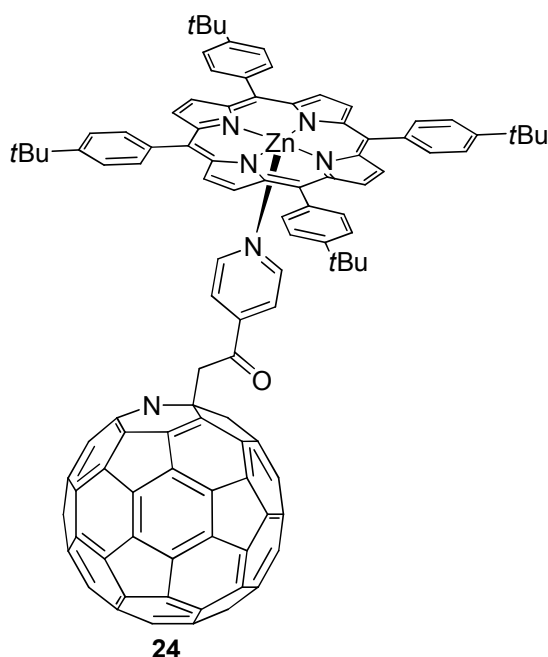
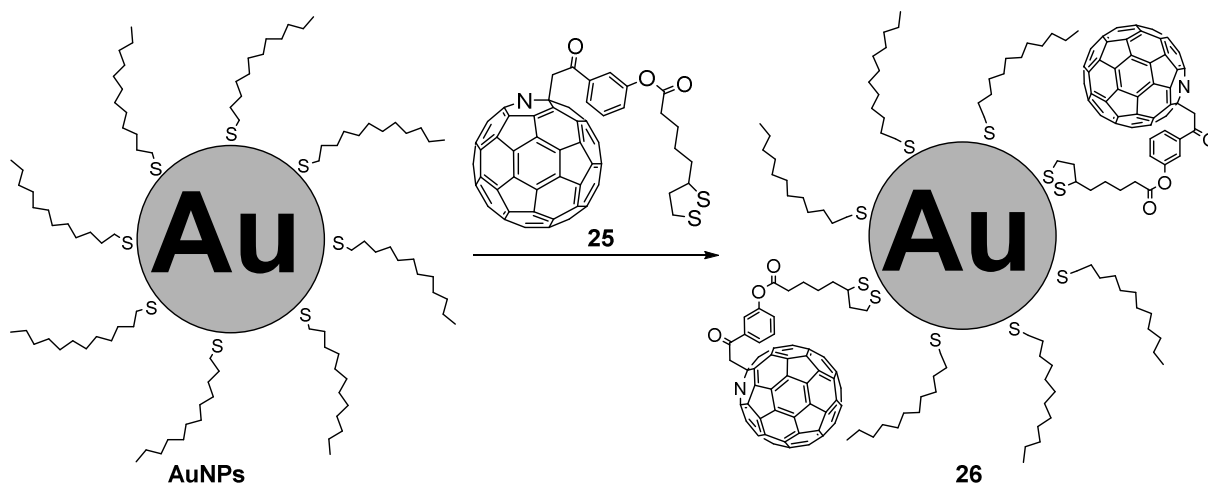


Figure 4. C₅₉N-porphyrin supramolecular dyad.

Finally, an organic-inorganic nanohybrid, where the azafullerene was decorated with gold nanoparticles, has been recently synthesized and its photophysical properties investigated.³⁵ At first, the dithiolane functionalized azafullerene **25** was synthesized in 85% yield from a condensation reaction between a phenolic C₅₉N derivative and lipoic acid. Nanohybrid **26** was then prepared by a ligand exchange reaction between dodecanethiol stabilized Au nanoparticles (AuNPs) and **25** (Figure 6). High-resolution transmission electron microscopy (HR-TEM)

images of **26** revealed a broad particle size distribution with two populations of 2.2 and 4.5 nm average particle size, in contrast to AuNPs where a narrow distribution centered at 2 nm was the case. Furthermore, a non-uniform electron density of the large nanoparticles in **26**, together with the presence of some aggregates, suggested an azafullerene-induced aggregation of nanoparticles towards large agglomerates. ^1H NMR measurements of **26** showed a 1.6% w/w loading of **25**. In the absorption spectrum, the surface plasmon band (SPB) of AuNPs was red-shifted in **26**, suggesting closer inter-particle proximity, while the small loading of **25** did not allow the characteristic azafullerene peaks to appear. Steady state fluorescence measurements showed a weak broad emission band at 805 nm, after excitation either at 330 nm (where azafullerene absorbs) or at 500 nm (negligible C_{59}N absorption) in toluene, blue-shifted and enhanced relative to that of an equimolar C_{59}N solution of **25**, suggesting energy transfer from AuNPs to C_{59}N . Transient absorption measurements showed that after excitation, together with the AuNPs excitation relaxation (2.5 ps), a non-intense absorption appears, which is attributed to $\text{C}_{59}\text{N}^{1\text{S}}$, indicative of energy transfer.



Scheme 4. Preparation of C_{59}N decorated with gold nanoparticles.

4. Conclusions

The preparation of azafullerene-based donor-acceptor systems via the two main functionalization strategies, electrophilic aromatic substitution and Mannich type reactions, has been reviewed. The variety of common functional groups that the donor can bear (acetyl, aryl, hydroxyl, amino, carboxy) to react with the bisazafullerene (or a simple azafullerene derivative), facilitates access to the desirable dyads. Although relatively few, azafullerene-based donor-acceptor systems show interesting properties on intra-molecular energy or electron transfer. In particular, owing to the low energy of azafullerene singlet excited state, a fast (ultra-fast in many cases) energy transfer

from the donor excited state is commonly observed in non-polar media, although charge transfer has also been detected. On the other hand, in polar media, stabilization of the charge-separated state leads to the formation of radical ion-pairs. In any case, energy or charge transfer to C₅₉N is the preferred option for the deactivation of the donor excited state. Without doubt, this particular research area can be further expanded when considering the possibility of incorporating multichromophoric arrays of diverse electron donors to azafullerene.

5. References

1. Hummelen, J. C.; Knight, B.; Pavlovich, J.; González, R.; Wudl, F. *Science* **1995**, 269, 1554.
<http://dx.doi.org/10.1126/science.269.5230.1554>
2. Xie, R.-H.; Bryant, G. W.; Sun, G.; Kar, T.; Chen, Z.; Smith, V. H.; Araki, Y.; Tagmatarchis, N.; Shinohara, H.; Ito, O. *Phys. Rev. B* **2004**, 69, 201403.
<http://dx.doi.org/10.1103/PhysRevB.69.201403>
3. Wessendorf, C. D.; Eigler, R.; Eigler, S.; Hanisch, J.; Hirsch, A.; Ahlswede, E. *Sol. Energy Mater. Sol. Cells* **2015**, 132, 450.
<http://dx.doi.org/10.1016/j.solmat.2014.09.038>
4. Xiao, Z.; He, D.; Zuo, C.; Gan, L.; Ding, L. *RSC Adv.* **2014**, 4, 24029.
<http://dx.doi.org/10.1039/c4ra02757d>
5. Vostrowsky, O.; Hirsch, A. *Chem. Rev.* **2006**, 106, 5191.
<http://dx.doi.org/10.1021/cr050561e>
6. Hirsch, A.; Nuber, B. *Acc. Chem. Res.* **1999**, 32, 795.
<http://dx.doi.org/10.1021/ar980113b>
7. Hummelen, J.; Bellavia-Lund, C.; Wudl, F. In *Topics in Current Chemistry: Fullerenes and Related Structures*; Hirsch, A., Ed.; Springer Berlin Heidelberg: 1999; Vol. 199, p 93.
http://dx.doi.org/10.1007/3-540-68117-5_3
8. Hummelen, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, 117, 7003.
<http://dx.doi.org/10.1021/ja00131a024>
9. Reuther, U.; Hirsch, A. *Carbon* **2000**, 38, 1539.
[http://dx.doi.org/10.1016/S0008-6223\(00\)00053-1](http://dx.doi.org/10.1016/S0008-6223(00)00053-1)
10. Hirsch, A.; Brettreich, M. *Fullerenes – Chemistry and Reactions*; Wiley-VCH Verlag, Weinheim, 2005; pp 289–302.
<http://dx.doi.org/10.1002/3527603492.ch10>
11. Hauke, F.; Hirsch, A. *Chem. Commun.* **2001**, 1316.
<http://dx.doi.org/10.1039/b103169b>
12. Bellavia-Lund, C.; González, R.; Hummelen, J. C.; Hicks, R. G.; Sastre, A.; Wudl, F. *J. Am. Chem. Soc.* **1997**, 119, 2946.
<http://dx.doi.org/10.1021/ja964447c>
13. Vougioukalakis, G. C.; Orfanopoulos, M. *Tetrahedron Lett.* **2003**, 44, 8649.

- <http://dx.doi.org/10.1016/j.tetlet.2003.09.158>
14. Tzirakis, M. D.; Orfanopoulos, M. *Chem. Rev.* **2013**, *113*, 5262.
<http://dx.doi.org/10.1021/cr300475r>
15. Hauke, F.; Hirsch, A. *Tetrahedron* **2001**, *57*, 3697.
[http://dx.doi.org/10.1016/S0040-4020\(01\)00235-6](http://dx.doi.org/10.1016/S0040-4020(01)00235-6)
16. Nuber, B.; Hirsch, A. *Chem. Commun.* **1998**, 405.
<http://dx.doi.org/10.1039/a707704a>
17. Hauke, F.; Hirsch, A. *Chem. Commun.* **1999**, 2199.
<http://dx.doi.org/10.1039/a906711f>
18. Vougioukalakis, G. C.; Orfanopoulos, M. *J. Am. Chem. Soc.* **2004**, *126*, 15956.
<http://dx.doi.org/10.1021/ja045495x>
19. Roubelakis, M. M.; Vougioukalakis, G. C.; Nye, L. C.; Drewello, T.; Orfanopoulos, M. *Tetrahedron* **2010**, *66*, 9363.
<http://dx.doi.org/10.1016/j.tet.2010.10.006>
20. Guldi, D.; Hauke, F.; Hirsch, A. *Res. Chem. Intermed.* **2002**, *28*, 817.
<http://dx.doi.org/10.1163/15685670260469438>
21. Hauke, F.; Vostrowsky, O.; Hirsch, A.; Quaranta, A.; Leibl, W.; Leach, S.; Edge, R.; Navaratnam, S.; Bensasson, R. V. *Chem. Eur. J.* **2006**, *12*, 4813.
<http://dx.doi.org/10.1002/chem.200501536>
22. Tagmatarchis, N.; Shinohara, H. *Org. Lett.* **2000**, *2*, 3551.
<http://dx.doi.org/10.1021/ol0002121>
23. Tagmatarchis, N.; Shinohara, H.; Fujitsuka, M.; Ito, O. *J. Org. Chem.* **2001**, *66*, 8026.
<http://dx.doi.org/10.1021/jo0104678>
24. Eigler, R.; Heinemann, F. W.; Hirsch, A. *Chem. Commun.* **2014**, *50*, 2021.
<http://dx.doi.org/10.1039/c3cc48461k>
25. Hauke, F.; Herranz, M. A.; Echegoyen, L.; Guldi, D.; Hirsch, A.; Atalick, S. *Chem. Commun.* **2004**, 600.
<http://dx.doi.org/10.1039/b315006b>
26. Hauke, F.; Hirsch, A.; Liu, S.-G.; Echegoyen, L.; Swartz, A.; Luo, C.; Guldi, D. M. *ChemPhysChem* **2002**, *3*, 195.
[http://dx.doi.org/10.1002/1439-7641\(20020215\)3:2<195::AID-CPHC195>3.0.CO;2-C](http://dx.doi.org/10.1002/1439-7641(20020215)3:2<195::AID-CPHC195>3.0.CO;2-C)
27. Hauke, F.; Atalick, S.; Guldi, D. M.; Mack, J.; Scott, L. T.; Hirsch, A. *Chem. Commun.* **2004**, 766.
<http://dx.doi.org/10.1039/b316139k>
28. Hauke, F.; Hirsch, A.; Atalick, S.; Guldi, D. *Eur. J. Org. Chem.* **2005**, 1741.
<http://dx.doi.org/10.1002/ejoc.200400771>
29. Hauke, F.; Atalick, S.; Guldi, D. M.; Hirsch, A. *Tetrahedron* **2006**, *62*, 1923.
<http://dx.doi.org/10.1016/j.tet.2005.04.078>
30. Rotas, G.; Ranta, J.; Efimov, A.; Niemi, M.; Lemmetyinen, H.; Tkachenko, N.; Tagmatarchis, N. *ChemPhysChem* **2012**, *13*, 1246.

<http://dx.doi.org/10.1002/cphc.201101029>

31. Lemmetyinen, H.; Kumpulainen, T.; Niemi, M.; Efimov, A.; Ranta, J.; Stranius, K.; Tkachenko, N. V. *Photochem. Photobiol. Sci.* **2010**, 9, 949.

<http://dx.doi.org/10.1039/c0pp00059k>

32. Rotas, G.; Charalambidis, G.; Glatzl, L.; Gryko, D. T.; Kahnt, A.; Coutsolelos, A. G.; Tagmatarchis, N. *Chem. Commun.* **2013**, 49, 9128.

<http://dx.doi.org/10.1039/c3cc45191g>

33. Hauke, F.; Swartz, A.; Guldi, D. M.; Hirsch, A. *J. Mater. Chem.* **2002**, 12, 2088.

<http://dx.doi.org/10.1039/b202060b>

34. Da Ros, T.; Prato, M.; Guldi, D. M.; Ruzzi, M.; Pasimeni, L. *Chem. Eur. J.* **2001**, 7, 816.

[http://dx.doi.org/10.1002/1521-3765\(20010216\)7:4<816::AID-CHEM816>3.0.CO;2-A](http://dx.doi.org/10.1002/1521-3765(20010216)7:4<816::AID-CHEM816>3.0.CO;2-A)

35. Rotas, G.; Niemi, M.; Tkachenko, N. V.; Zhao, S.; Shinohara, H.; Tagmatarchis, N. *Chem. Eur. J.* **2014**, 20, 14729.

<http://dx.doi.org/10.1002/chem.201403517>

Authors



Georgios Rotas was born in Athens in 1977, obtained his BSc on chemistry in 1998 and PhD degree on organic synthesis in 2005 from the University of Ioannina. In 2006 he joined the group of Dr. N. Tagmatarchis at the Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, and his research interests fall in the design, synthesis and study of electroactive fullerene, azafullerene and graphene-based materials.



Nikos Tagmatarchis is Director of Research in the Theoretical and Physical Chemistry Institute at the National Hellenic Research Foundation, in Athens, Greece. His research interests focus on the chemistry of carbon-based nanostructured materials in the context of electron transfer processes for diverse nanotechnological applications. His accomplishments in the area are reflected in a plethora of publications, citations and numerous invitations at conferences. He was recipient of the European Young Investigator Award (2004), Visiting Professor at the Chinese Academy of Sciences (2011) and Invited Fellow by the Japan Society for the Promotion of Science in Japan (2012-2013).