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# Novel electron-deficient oligo(phenyleneethynylene) derivatives for molecular electronics

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ABSTRACT

This work reports synthesis and characterizations of two new electron-poor "oligo(phenyleneethynylene) (OPE) type" molecular wires for fundamental studies of electron transport in molecular junctions. These OPE derivatives display three aromatic rings functionalized (i) with NO_2 (**OPN**) or fluorine (**OPF**) groups on the central aryl core and (ii) with the requisite protected thiolate anchoring groups on the lateral rings at both ends. We show that the moderately effective Sonogashira couplings can give access to such rare electrodeficient molecules but are unfortunately associated with significant side reactions. We detail the choice of adequate reaction conditions to allow the recovery of suitable amounts of compounds bearing several strongly electron-withdrawing substituents on their central ring for further study of the physical properties.

GRAPHICAL ABSTRACT
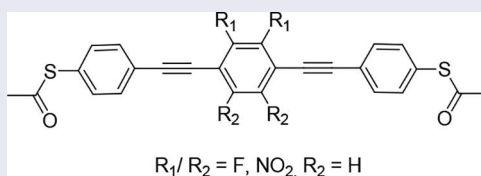
$R_1/R_2 = F$, NO_2, $R_2 = H$

Introduction

During the past decades, oligo(phenyleneethynylene) (OPE) derivatives have emerged as benchmark molecules for studying charge transport in molecular junctions.[1–3] Indeed, following the "bottom-up" approach expressed by Feynman proposing that atoms can be arranged in a manner to build circuits of a few thousands of Angströms across,[4] single molecules as active elements have been considered as potential building blocks for future nanoelectronic systems because of their advantages on cost, scalability, component density, and power consumption.[1,5,6] In that context, the attractiveness of OPEs lies in their rigid, rod-like structure with extended π-conjugation through the backbone leading to high conductivity and other electrical properties such as negative differential resistance or molecular

switching that can be systematically tuned by chemical design. Such a tuning is particularly important to achieve controllable properties by choosing the appropriate chemical functions, which allow infinite possibilities of developments toward the preparation of molecular devices with efficient performances. In our group, we participated to such studies by probing the electrical conductivity of metal-containing OPE derivatives and by establishing that insertion of ruthenium atoms in the backbone provides interestingly higher conductance over pure organic OPEs.[7]

Basically, a molecular wire consists in a molecular chain that provides strong electrode coupling between two electrodes attached to its chain ends to promote electron transfer through this bridge. The exploration of charge transport properties has been conducted with a wide range of molecules using various techniques (mechanical break junctions, scanning probe microscopies, nanogaps …) to understand the structure/property relationship.[8] Various factors are known to affect the electrical properties of a typical molecular junction such as the alignment between the Fermi level of the electrodes and the frontier orbitals of the molecule. Recently, many efforts have been devoted to gain a better understanding by rationalizing the impact of bridging molecule structures on the resulting electronics and current–voltage characteristics of the molecular junctions by revisiting simple molecular wires.[9,10] In that respect, εh, the key offset of the appropriate molecular orbital energy relative to the electrode Fermi level used to simulate the I–V curves can be tuned by changing (i) the contact terminal groups, (ii) the electrodes work functions, and (iii) the electronic structure of the molecules.[9]

In this context and following the chemical potential equalization principle allowing to establish the existence or not of a so-called Fermi level pinning phenomenon (i.e., same alignment of relevant molecular orbitals in the junction in spite of a varying ionization potentials in isolated compounds), the precise investigation of organic OPE derivatives is particularly attractive.[9–11] Indeed, a minimum number of synthetic steps will give access to a wide range of molecules likely to display different ionization potentials, to show that εh for the molecule inserted between electrodes can indeed differ largely from the one of the same molecules in its isolated state. This can be reached by varying the donor and/or acceptor strengths on phenyl rings on the backbone. However, surprisingly, OPE derivatives bearing strongly electron-withdrawing substituents and protected thiolate anchoring groups are extremely rare,[12] owing to the modest reactivity of the involved alkyne reagents and highly deleterious side reactions. Therefore, in the course of our current work aiming at (re-)investigating the electrical conductivity of several OPEs with three aryl groups and different HOMO levels,[13] we report the synthesis of two original highly electron-poor OPE molecules incorporating NO_2 groups or fluorine atoms on the aryl central core and bearing protected thiolate anchoring groups at both ends of the molecule.

Results and discussion

The two targeted compounds are derivative of the ubiquitous OPE compound constituted of three aryl group. The central aromatic ring is substituted with four fluorine atoms or two nitro groups in the *ortho* and *para* positions (Chart 1).

OPE was previously obtained by Tour et al.[14] from 1,4-diodobenzene by Sonogashira coupling with S-(4-ethynylphenyl)ethanethioate. By adjusting the nature of this central
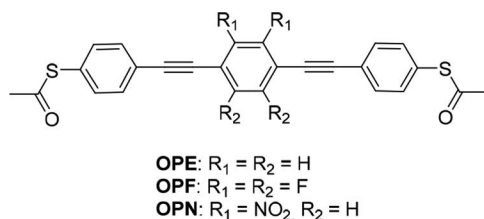
OPE: $R_1 = R_2 = H$
OPF: $R_1 = R_2 = F$
OPN: $R_1 = NO_2, R_2 = H$

Chart 1. Target compounds.

core, i.e., with 1,4-diiodo-tetrafluorobenzene in this case, this route presents the advantage of potentially afford several OPE analogues with a different central core in one step only. The modest ability of 1,4-diiodo-tetrafluorobenzene to undergo Sonogashira coupling with electron-rich terminal alkynes was already highlighted in similar coupling involving p-OMe- or p-NMe$_2$-substituted phenyl acetylenes, and affording the corresponding OPEs in ca. 41% yield.[15] To complement these results, the monocoupling compound obtained from 1,4-diiodo-tetrafluorobenzene and S-(4-ethynylphenyl)ethanethioate was recently reported in moderate yield (25% yield) again confirming this tendency.[16] Herein, the preparation of **OPF** was similarly attempted from 1,4-diiodo-tetrafluorobenzene in the presence of a twofold excess of S-(4-ethynylphenyl)ethanethioate[17] (2.2 Eq.). The reaction was performed in degazed Et$_3$N, at room temperature, in the presence of PdCl$_2$(PPh$_3$)$_2$ catalyst (4 mol%) and CuI (20 mol%) (Scheme 1) for 2 days. Rerun of the reaction in the crude was required with a second addition of equivalent amount of catalyst and CuI after 24 h. TLC and NMR monitoring of the reaction clearly indicated the full consumption of S-(4-ethynylphenyl)ethanethioate, whereas some diiodo-tetrafluorobenzenes were recovered. They also revealed that at least two other products are present, the monosubstituted intermediate and the homocoupling derivative, respectively. The ^{19}F NMR spectrum of the crude shows a set of characteristic signals clearly indicating the presence of starting aryl-iodide, monosubstituted compound, and **OPF** in a 2/3/3 ratio, respectively. Although the first coupling takes place in a reasonable amount, the second one appears less effective and the homocoupling process takes place at the expense of desired cross-coupling reactions that seem kinetically disfavored, a fact we often observed with the electron-rich S-(4-ethynylphenyl)ethanethiolate.

Indeed, with electron-rich aryl acetylenes, coupling reactions are slower than those with precursors bearing electron-withdrawing substituents which are known to undergo faster coupling reaction rate than oxidation of Pd^0 by the surrounding medium.[18] Thus, since the reaction setup is not completely dioxygen free, homocoupling might be highly promoted with this electron-rich aryl acetylenes. In addition, those alkynes are also
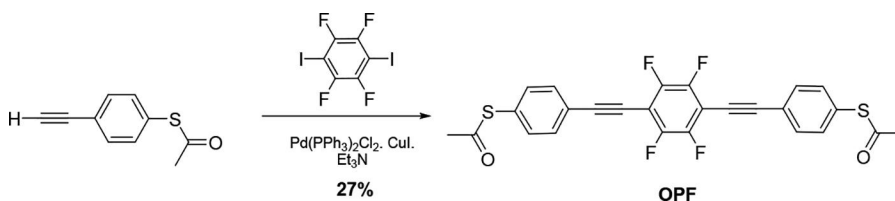
Scheme 1. Synthesis path yielding **OPF**.

hypothesized to induce gentle formation of Pd-alkyne complexes that could further favor homocoupling in slow reactions.[19] Finally, the deprotonation of the alkyne can also be critical to slow down the overall process.[20]

Hence, after optimization, the targeted **OPF** was obtained in 27% isolated yield. The moderate solubility of **OPF** in common organic solvents is worth noting, as it probably also contributes to the poor isolated yield displayed in this study.

The structure of **OPF** was ascertained by NMR spectroscopy. The ^{19}F NMR spectrum shows a singlet at −136.7 ppm corresponding to the four equivalent fluorine atoms. The ^{1}H NMR spectrum displays two characteristic deshielded doublets[16] at $\delta = 7.63$ ppm and 7.45 ppm ($^{3}J_{HH} = 8.20$ Hz) for the aryl moieties bearing the thioacetate groups that resonate as a singlet at $\delta = 2.44$ ppm, all consistent with the **OPF** molecular structure.[16] Finally, in the ^{13}C NMR spectrum, the characteristic C−F carbon atom resonance is observed at 146.6 ppm ($^{1}J_{CF} = 250$ Hz). The compound was also unambiguously identified by high-resolution mass spectra (HRMS) techniques.

Sonogashira reactions with aryl nitro units are also known to be problematic, and several side products are often observed.[21] Best conditions for these aromatic compounds require moderate temperatures, short reaction times, and, in particular, the use of a base in low concentration.[22] For example, substitution of nitro groups by a base has been reported,[12] especially with two nitro groups on the same aromatic ring, and very recently it has been shown that Pd^{0} catalyzes in fact the cleavage of Ar−NO$_2$ bonds.[23] Also, the proximity of the acetylene in ortho position of the nitro group assists the formation of 2-aryl-3H-indol-3-one N-oxides, a nitrogen heterostructure.[24]

At first glance, in the light of this facts, we planned to obtain **OPN** using the previous method, i.e., from S-(4-ethynylphenyl)ethanethioate and 1,4-dibromo-2,3-dinitrobenzene by trying different Pd catalysts (PdCl$_2$(Ph$_3$)$_2$, Pd(Ph$_3$)$_4$, Pd$_2$(dba)$_3$) and different bases (diisopropylethyl amine, triethylamine) in a mixture with THF. Unfortunately, the formation of **OPN** was not observed from the thin-layer chromatography and from ^{1}H NMR spectroscopy. After workup, only few starting 1,4-dibromo-2,3-dinitrobenzene was recovered along with the compound resulting from homocoupling of the terminal alkyne. Unidentified products probably resulting from side reactions mentioned above were also present. This evidences again the relatively low efficiency of the coupling, which is not compatible with the low temperatures and short reaction time requirements for nitro aromatics to avoid degradation products.

We then turned into the strategy consisting in preparing first the diethynyl central core for a further coupling reaction with 1-iodo-4-thioacetyl benzene (Scheme 2). This strategy
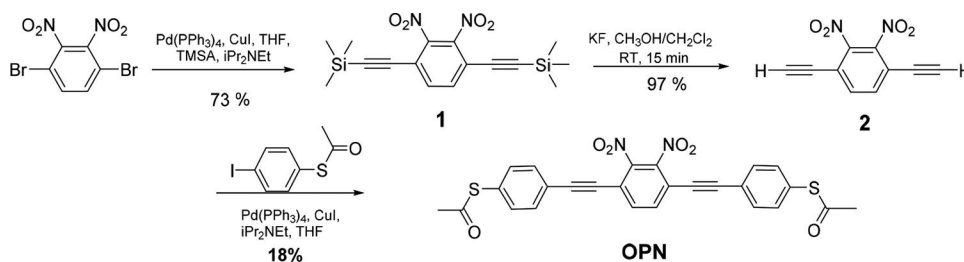
Scheme 2. Synthesis path yielding **OPN**.

allowed Tour's group to obtain the mono nitro analog[22] and Mayor's group to achieve the synthesis of macrocyclic molecular rods from macrocycles incorporating ortho-dinitro phenyl units.[21] Compound **1** bearing two protected alkyne functions was then prepared according to the Mayor's procedure from 1,4-dibromo-2,3-dinitrobenzene by Sonogashira coupling reaction with trimethylsilylacetylene, in the presence of $Pd(PPh_3)_4$/CuI and diisopropylethylamine.[21] We noticed that the choice of diisopropylethylamine as the base is crucial. With different amines such as diisopropylamine or triethylamine, severe degradation of the central aromatic core is observed (*vide supra*). Thus, in these conditions, product **1** was isolated in 73% yield and the TMS groups were readily removed using 2 Eq. of potassium fluoride in a mixture of methanol/dichloromethane to afford 1,4-diethynyl-2,3-dinitrobenzene (**2**) in 97% isolated yield.

Compound **2** was then further reacted with an excess of 1-iodo-4-thioacetyl benzene in another Sonogashira cross-coupling reaction using a high loading of 50% $Pd(PPh_3)_4$ catalyst with respect to the aryl iodide and in the presence of a few amount of base. This palladium loading was used to accelerate the reaction and promote the coupling reaction over side reactions including homocoupling reaction and degradations of **2**. Similar degradations than those observed with the first strategy and involving nitro groups are however observed but to a lesser extent here. Therefore, within 4 h, alkyne precursor **2** is consumed and a large amount of unreacted 1-iodo-4-thioacetyl benzene is observed in the crude along with the unidentified degradation products detected in the aromatic region of ^{1}H NMR spectrum. These reaction conditions represent the best compromise we could find, and the target molecular wire **OPN** was obtained with a moderate 18% isolated yield (see "Experimental" section). **OPN** was fully characterized by NMR spectroscopy. The ^{1}H NMR spectrum shows a singlet at $\delta = 2.45$ ppm for the methyl groups and a singlet at $\delta = 7.77$ ppm integrating for two hydrogen atoms corresponding to the two central aromatic hydrogen atoms. The signals for the other aromatic protons are seen in **OPN** as two separated slightly upfield doublets at $\delta = 7.57$ ppm ($J = 8.12$ Hz) and 7.46 ppm ($J = 8.16$ Hz).

Preliminary studies on the optical properties of **OPE** and **OPF** show that the electron-withdrawing character of fluoro and nitro groups clearly influences the energy levels of the frontier orbitals with respect to **OPE**, as expected. Indeed, in the UV–vis spectra (see Supplementary information), the observed shifts of the main electronic transition of **OPE** from 333 to 340 and 348 nm in **OPF** and **OPN**, respectively, and their shape modifications are characteristic of the lower energy of the transitions to the first singlet excited states in **OPF** and **OPN**. A full rationalization of the physical and electrical properties of these new electron-poor OPEs will be reported in due course.[13]

Conclusion

In this report, we present the synthesis and characterization of two new electron-poor "OPE-type" molecular wires substituted with NO_2 (**OPN**) and fluoro (**OPF**) groups on the central aromatic core. The moderately efficient Sonogashira couplings giving access to these molecules associated to various significant side reactions are unfortunately detrimental to the reaction efficiency. Nevertheless, we found that an accurate choice of the reaction conditions allows to perform the synthesis and to obtain such very rare thiolate-terminated compounds bearing several strongly electron-withdrawing groups.

Importantly, even if the yields are modest, these reaction conditions allow the recovery of an accurate amount of compounds for further physical studies to rationalize an operating pinning of the relevant orbital of these molecules (HOMO) to the Fermi level of the electrodes in molecular junctions.

Experimental part

General

All reactions were achieved under an inert atmosphere, using the Schlenk techniques. Solvents were freshly distillated under argon using standard procedures. S-(4-ethynylphenyl) ethanethioate) and S-(4-iodophenyl)ethanethioate were prepared as previously reported.[17] NMR spectra were recorded on a Bruker AVANCE I 500 MHz spectrometer or a Bruker AVANCE III 400 MHz spectrometer. IR spectra were recorded on a IFS 28 Brucker spectrometer using KBr pellets or ATR. HRMS were recorded in Rennes at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO) on a Bruker MicrO-Tof-Q II spectrometer.

Procedure for OPF

1,2,4,5-tetrafluoro-3,6-diiodobenzene (125 mg, 0.309 mmol, 1 Eq.), S-(4-ethynylphenyl) ethanethioate) (120 mg, 0.682 mmol, 2.2 Eq.), $PdCl_2(PPh_3)_2$ (9 mg, 4 mol%), CuI (12 mg, 20 mol%) were added in a Schlenk tube and were pumped 45 min under vacuum. Then, distilled and thoroughly degassed Et_3N (6 mL) was added to the Schlenk tube at 0 °C. The suspension was then allowed to stir vigorously for 24 h at 50 °C. The reaction was quenched by removing the solvent under vacuum and the residue was taken up in diethyl ether and filtered over a pad of celite. The solvents were removed. The crude was pumped under vacuum 45 min and the previous synthetic procedure was repeated again on the crude with the same amount of catalysts: $PdCl_2(PPh_3)_2$ (9 mg, 4 mol%), CuI (12 mg, 20 mol%). After 24 h stirring at 50 °C, the solvent was removed and the residue was taken up and filtered with diethylether over a pad of celite. Purification by column chromatography with silica gel (petroleum ether/dichloromethane (8:2)) afforded several fractions. The third one contained a mixture of OPF and the homocoupling adduct. A second purification on this fraction with silica gel (diethyl ether/pentane (4:96) to MeOH/diethyl ether (1:10)) afforded 42 mg (27%) of **OPF** as a white solid. ^1H NMR (400 MHz, ppm, $CDCl_3$): $\delta = 2.44$ (s, 6H, CH_3), 7.45 (d, $^3J_{HH} = 8.2$ Hz, 4H, C_6H_4), 7.63 (d, $^3J_{HH} = 8.2$ Hz, 4H, C_6H_4). ^{19}F NMR (376.5 MHz, ppm, $CDCl_3$): $\delta = -136.78$. ^{13}C NMR (100 MHz, ppm, $CDCl_3$): $\delta = 192.9$ (C=O), 146.6 (d, $^1J_{CF} = 250$ Hz, C-F), 134.3 (o-$C_6H_4SCOCH_3$), 132.5 (m-$C_6H_4SCOCH_3$), 130.0 (C-S), 122.6 ($\underline{C}$-C≡C), 102.2 (-C≡$\underline{C}$-C_6F_4), 76.1 (-$\underline{C}$≡C-C_6F_4), 30.4 (SCO$\underline{C}H_3$). UV-vis (CH_2Cl_2): $\lambda_{max} = 339$ nm. FTIR (cm^{-1}, ATR) = 2967, 2916, 2847 (υ_{C-H}); 2226, 2207 ($\upsilon_{C≡C}$); 1695 ($\upsilon_{C=O}$); 1483 ($\upsilon_{C = C}$). HRMS FAB^+ (m/z): 521.0264 (calcd: 521.02636, ($[M + Na]^+$).

Procedure for OPN

1,4-diethynyl-2,3-dinitrobenzene (125 mg, 0.578 mmol), S-(4-iodophenyl)ethanethioate (803.5 mg, 2.891 mmol), $Pd(PPh_3)_4$ (1.336 mg, 1.156 mmol), and CuI (11 mg, 0.057 mmol) were added in a Schlenk tube and pumped under vacuum. Then, distilled diisopropylethylamine (0.8 mL) and toluene (16 mL) were added to the reaction mixture. The reaction was allowed to stir for 4 h at room temperature. The mixture was evaporated to dryness, the

residue was taken up with diethylether and the solution was filtered. After evaporation and purification with silica gel (pentane/dichloromethane (1:1)), 55 mg (18%) of **OPN** was recovered as a white solid.^{1}H NMR (400 MHz, ppm, CDCl$_3$): $\delta = 2.45$ (s, 6H, CH$_3$), 7.45 (d, $^3J_{HH} = 8.2$ Hz, 4H, C$_6$H$_4$), 7.58 (d, $^3J_{HH} = 8.2$ Hz, 4H, C$_6$H$_4$), 7.80 (s, 2H, C$_6$H$_2$(NO$_2$)$_2$). ^{13}C NMR (400 MHz, ppm, CDCl$_3$): $\delta = 192.80$ (C=O), 135.05 (CH, C$_6$H$_2$), 134.30 (o-C$_6$H$_4$SCOCH$_3$), 132.66 (m-C$_6$H$_4$SCOCH$_3$), 130.60 (C-S), 121.96 (C$_q$, C$_6$H$_4$), 118.30 (C-C≡C), 99.69 and 82.83 (C≡C), 30.39 (CH$_3$). UV-vis (CH$_2$Cl$_2$): $\lambda_{max} = 348$ nm. FTIR (cm^{-1}, ATR) = 2958, 2922, 2851 (υ_{C-H}); 2212 ($\upsilon_{C≡C}$); 1694 ($\upsilon_{C=O}$); 1547 ($\upsilon_{C=C}$). HRMS FAB$^+$ (m/z): 539.0342 (calcd: 539.0345, ([M + Na]$^+$).

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References

[1] (a) Chen, J.; Reed, M. A.; Rawlett, A. M. J.; Tour, J. M. *Science* **1999**, *286*, 1550; (b) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; et al. *Science.* **2001**, *292*, 2303.

[2] (a) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791. James, D. K.; Tour, J. M. *Chem. Mater.* **2004**, *16*, 4423; (b) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537. Walzer, K.; Marx, E.; Greenham, N. C.; Less, R. J.; Raithby, P. R.; Stokbro, K. J. *Am. Chem. Soc.* **2004**, *126*, 1229.

[3] (a) Kushmerick, J. G.; Holt, D. B.; Pollack, S. K.; Ratner, M. A.; Yang, J. C.; Schull, T. L.; Naciri, J.; Moore, M. H.; Shashidhar, R. *J. Am. Chem. Soc.* **2002**, *124*, 10654; (b) Terao, J.; Tanaka, Y.; Tsuda, S.; Kambe, N.; Taniguchi, M.; Kawai, T.; Saeki, A.; Seki, S. *J. Am. Chem. Soc.* **2009**, *131*, 18046.

[4] Feynman, R. Plenty of Room at the Bottom. *Caltech Engineer. Sci.* **1960**, *23*(5), 22–36. http://www.zyvex.com/nanotech/feynman.html

[5] (a) Reed, M. A.; Lee, T. (Eds.). *Molecular Nanoelectronics*; American Scientific Publishers: Stevenson Ranch, CA, 2003; (b) Ratner, M. A. *Nat. Nanotechnol.* **2013**, *8*, 378.

[6] (a) Choi, S. H.; Kim, B.; Frisbie, C. D. *Science* **2008**, *320*, 1382; (b) Song, H.; Kim, Y.; Jang, Y. H.; Jeong, H.; Reed, M. A.; Lee, T. *Nature* **2009**, *462*, 1039.

[7] (a) Schwarz, F.; Kastlunger, G.; Lissel, F.; Egler-Lucas, C.; Semenov, S. N.; Venkatesan, K.; Berke, H.; Stadler, R.; Lortscher, E. *Nat. Nanotechnol.* **2016**, *11*, 170; (b) Liu, K.; Wang, X.; Wang, F. *ACS Nano* **2008**, *2*, 2315; (c) Kim, B.; Beebe, J. M.; Olivier, C.; Rigaut, S.; Touchard, D.; Kushmerick, J. G.; Zhu, X. Y.; Frisbie, C. D. *J. Phys. Chem. C* **2007**, *111*, 7521; (d) Luo, L.; Benameur, A.; Brignou, P.; Choi, S. H.; Rigaut, S.; Frisbie, C. D. *J. Phys. Chem. C* **2011**, *115*, 19955; (e) Mahapatro, A. K.; Ying, J. W.; Ren, T.; Janes, D. B. *Nano Lett.* **2008**, *8*, 2131; (f) Al-Owaedi, O. A.; Milan, D. C.; Oerthel, M.-C.; Bock, S.; Yufit, D. S.; Howard, J. A. K.; Higgins, S. J.; Nichols, R. J.; Lambert, C. J.; Bryce, M. R.; *J. Organometall.* **2016**, *35*, 2944.

[8] Xiang, D.; Wang, X.; Jia, C.; Lee, T.; Guo, X. *Chem. Rev.* **2016**, *116*, 4318.

[9] Xie, Z.; Baldea, I.; Smith, C. E.; Wu, Y.; Frisbie, C. D. *ACS Nano* **2015**, *9*, 8022.

[10] (a) Van Dyck, C.; Geskin, V.; Cornil, J. *Adv. Funct. Mater.* **2014**, *24*, 6154; (b) Van Dyck, C.; Ratner, M. A. *J. Phys. Chem. C* **2017**, *121*, 3013.

[11] (a) Sayed, S. Y.; Fereiro, J. A.; Yan, H.; McCreery, R. L.; Bergren, A. J. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 11498. (b) Lenfant, S.; Guerin, D.; Van, F. T.; Chevrot, C.; Palacin, S.; Bourgoin, J. P.; Bouloussa, O.; Rondelez, F.; Vuillaume, D. *J. Phys. Chem. B* **2006**, *110*, 13947.

[12] Sunde, C. J.; Johnson, G.; Kade, C. F. *J. Org. Chem.* **1939**, *4*, 548.

[13] Rodriguez-Gonzalez, A. S.; Xie, Z.; Galangau, O.; Selvanathan, P.; Norel, L.; Van Dyck, C.; Costuas, K.; Frisbie, D.; Rigaut, S.; Cornil, J. (submitted for publication).

[14] Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C.-W.; Chen, J.; Wang, W.; *Chem. Eur. J.* **2001**, *7*, 5118.

[15] Kulhanek, J.; Bures, F.; Pytel, O.; Pippig, F.; Danko, M.; Mikysek, T.; Padelkova, Z.; Ludwig, M. *J. Fluor. Chem.* **2014**, *161*, 15.

[16] Wolf, J.; Eberspacher, I.; Groth, U.; Huhn, T. *J. Org. Chem.* **2013**, *78*, 8366.

[17] Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376.

[18] Elangovan, A.; Wang, Y. H.; Ho, T. I. *Org. Lett.* **2003**, *5*, 1841.

[19] Ljungdahl, T.; Bennur, T.; Dallas, A.; Emtenäs, H.; Martensson, J. *Organometallics* **2008**, *27*, 2490.

[20] Schilz, M.; Plenio, H. *J. Org. Chem.* **2012**, *77*, 2798.

[21] Blaszezyk, A.; Chadim, M.; Hanisch, C. V.; Mayor, M. *Eur. J. Org. Chem.* **2006**, *2006*, 3809.

[22] Price, W. D.; Dirk, S. M.; Maya, F.; Tour, J. M. *Tetrahedron* **2003**, *59*, 2497.

[23] Yadav, M. R.; Nagaoka, M.; Kashihara, M.; Zhong, R.-L.; Miyazaki, T.; Sakaki, S.; Nakao, Y. *J. Am. Chem. Soc.* **2017**, *139*, 9423.

[24] Rosen, G. M.; Tsai, P.; Barth, E. D.; Dorey, G.; Casara, P.; Spedding, M.; Haplern, H. J. *J. Org. Chem.* **2000**, *65*, 4460.