Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Multivalent Fullerene/π-Extended TTF Electroactive Molecules –Non-Covalent Interaction with Graphene and Charge Transfer Implications

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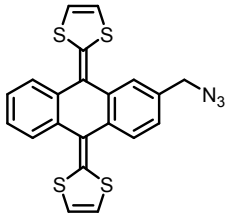
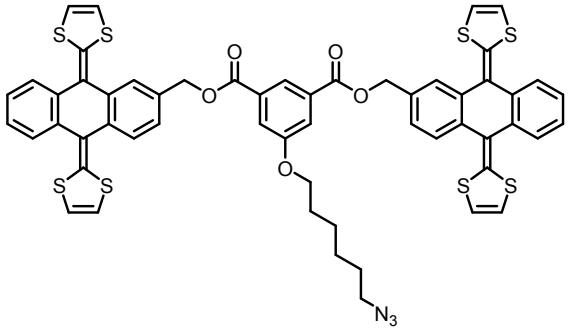
Chemical structures and characterization of new compounds

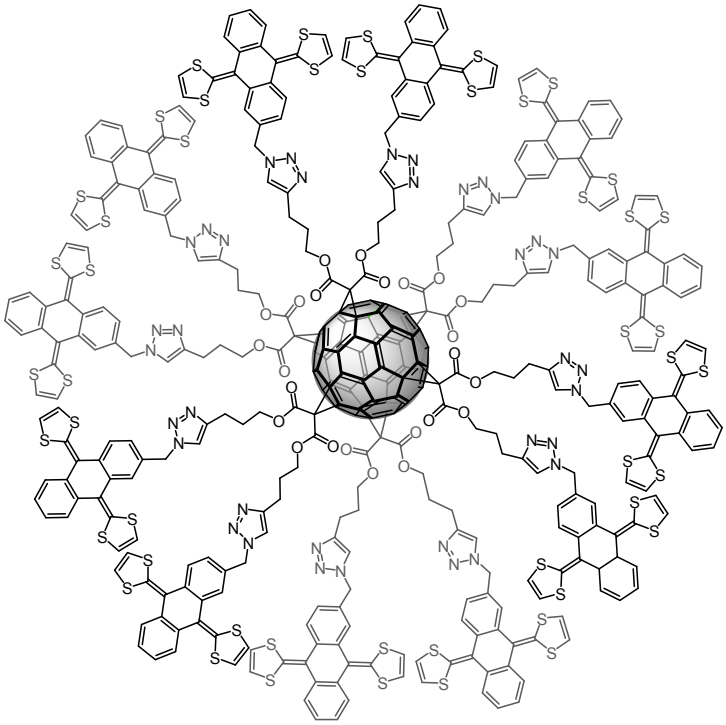
Compound 2a

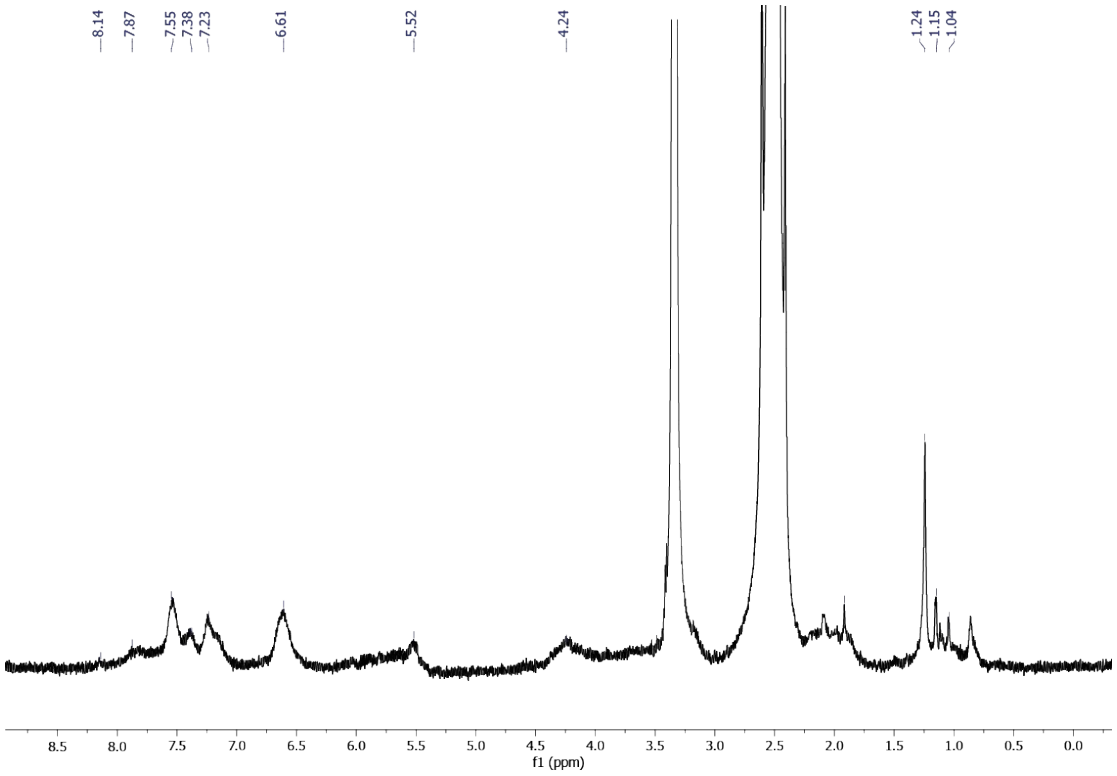


Compound 2b

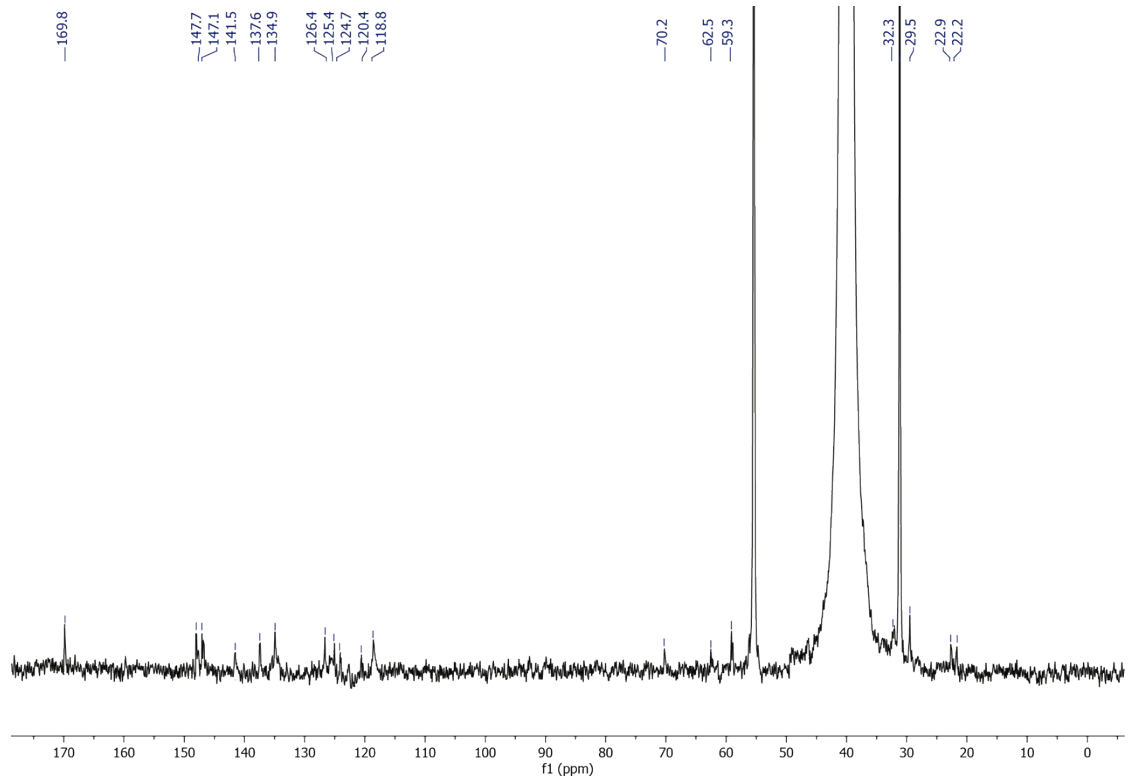


Compound 3a

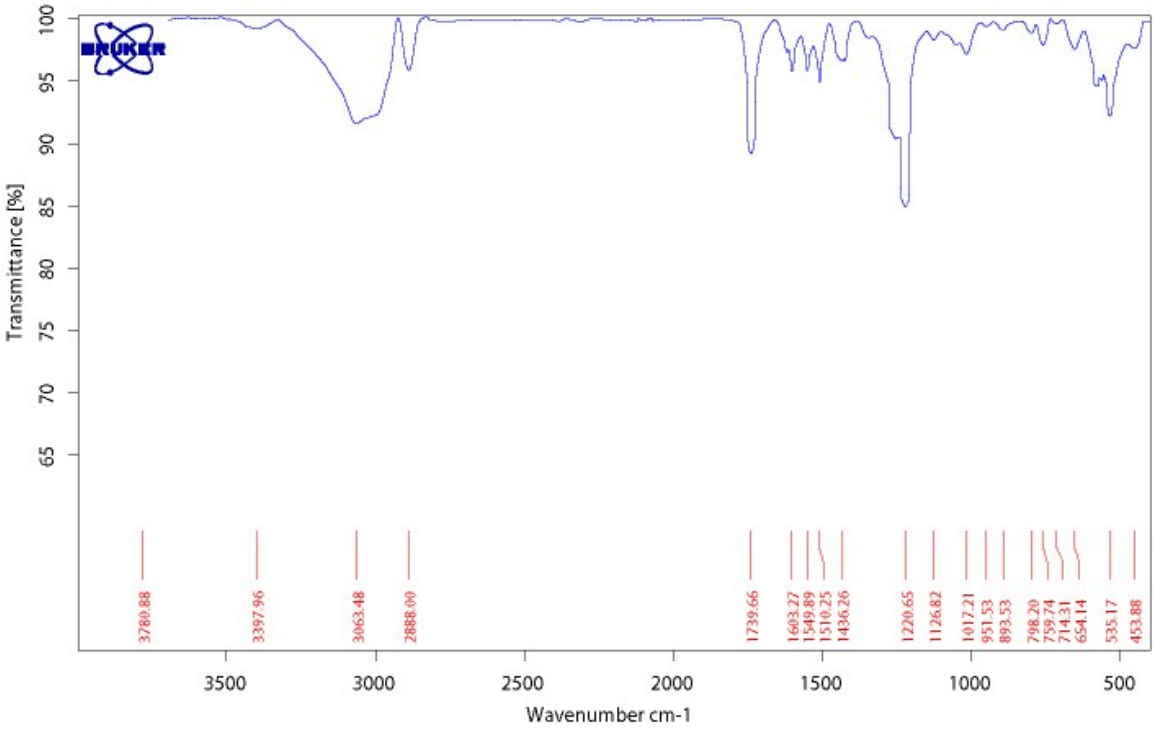




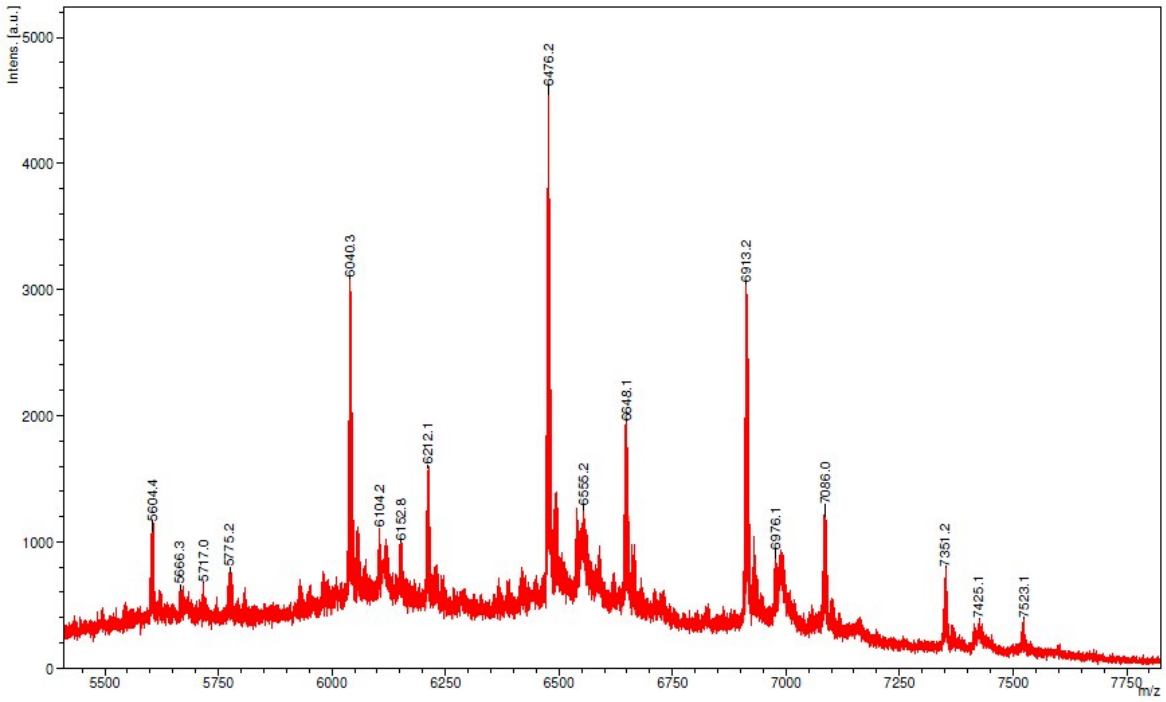
^{1}H NMR spectrum of **3a** (700 MHz, DMSO-d_6) at 298K.

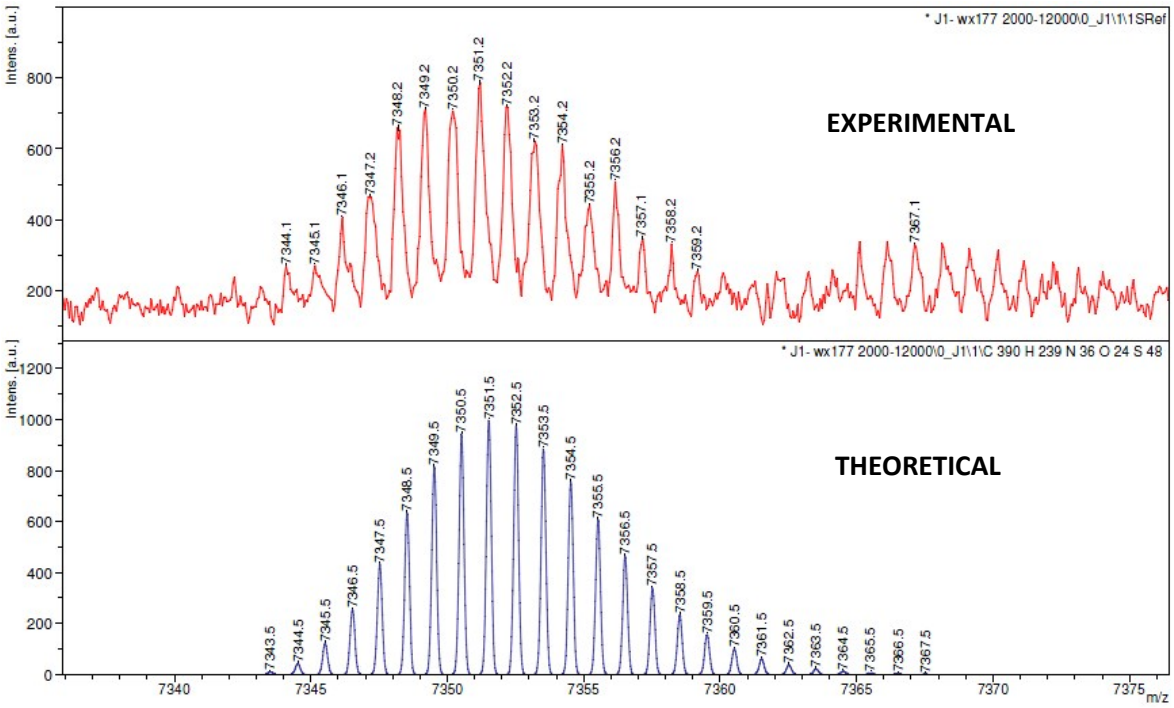


^{13}C NMR spectrum of **3a** (175 MHz, DMSO-d_6) at 298K.



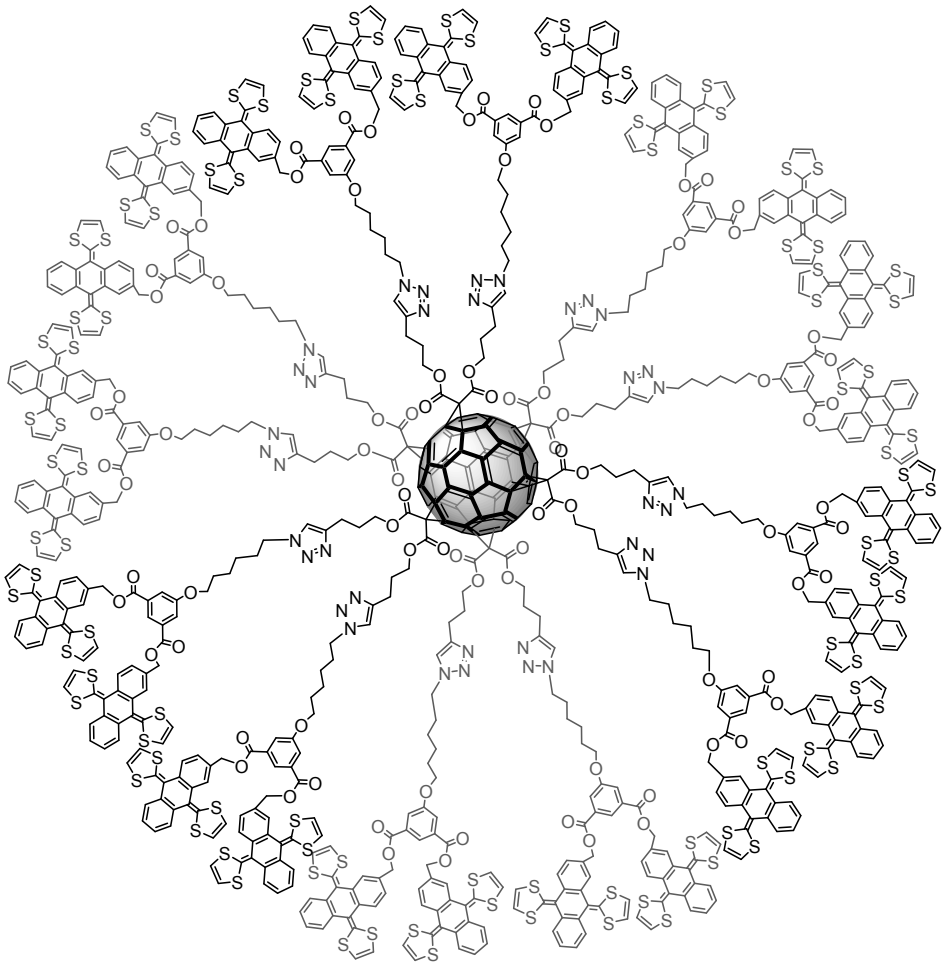
FTIR spectrum of **3a** showing the dissapearance of the signals of alkyne and azide groups present in the synthetic precursors.

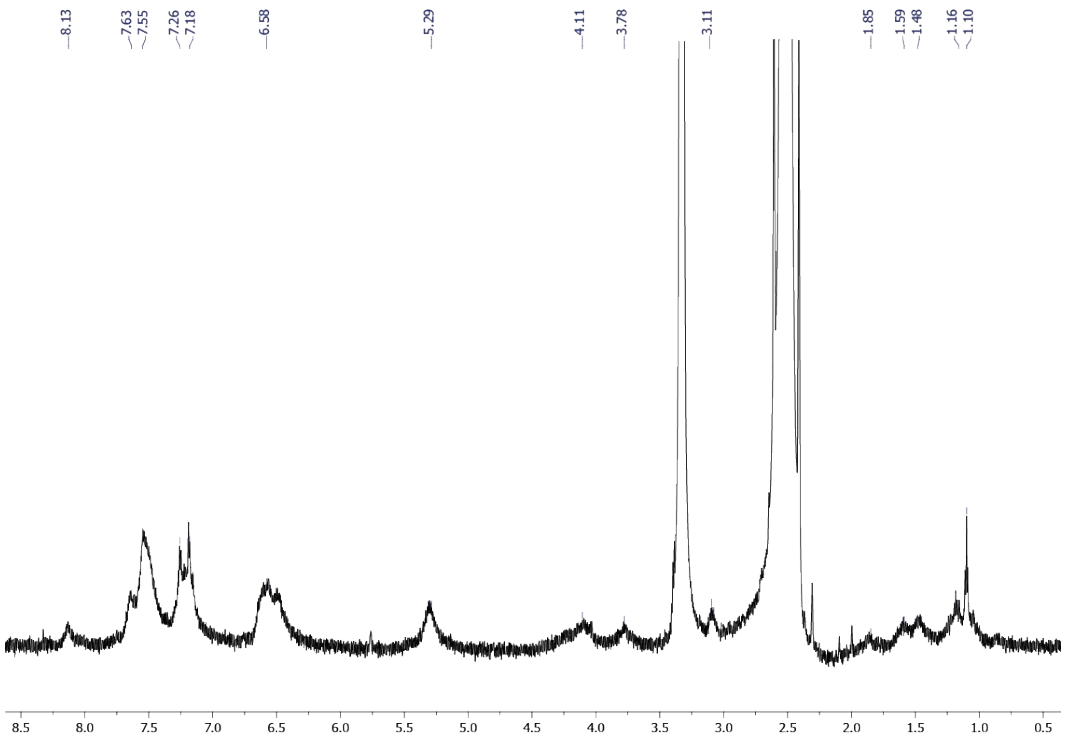




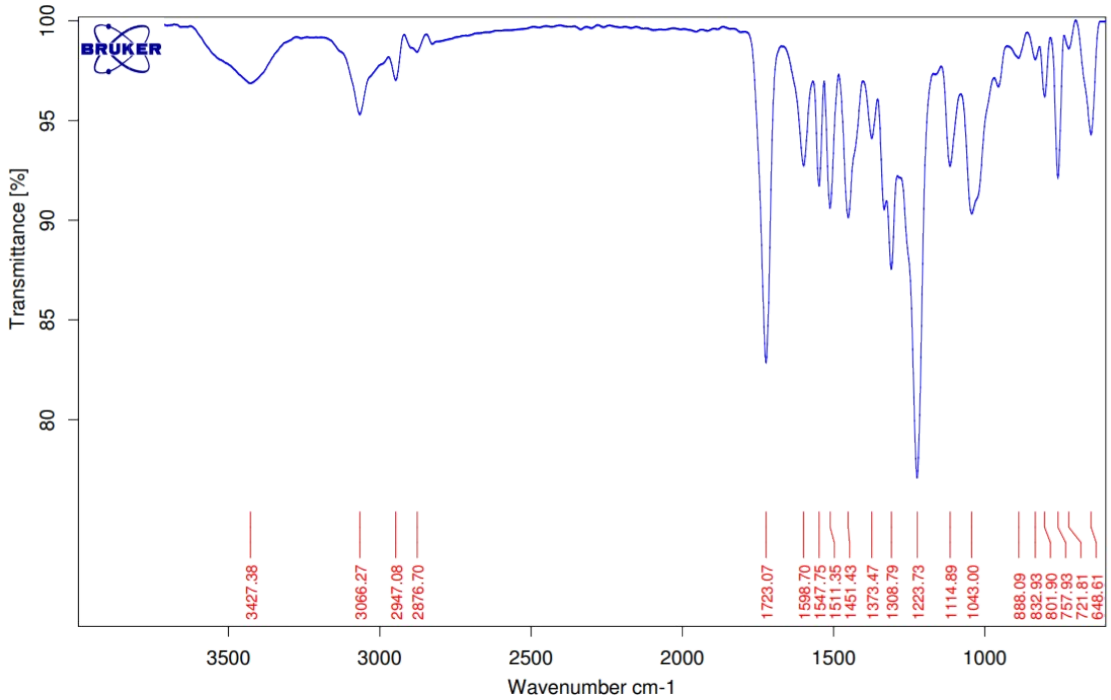
MS MALDI-TOF spectrum for **3a** and experimental *(up*) and theoretical (*down*) isotopic distribution for the molecular peak (7351.2 m/z).

Compound 3b

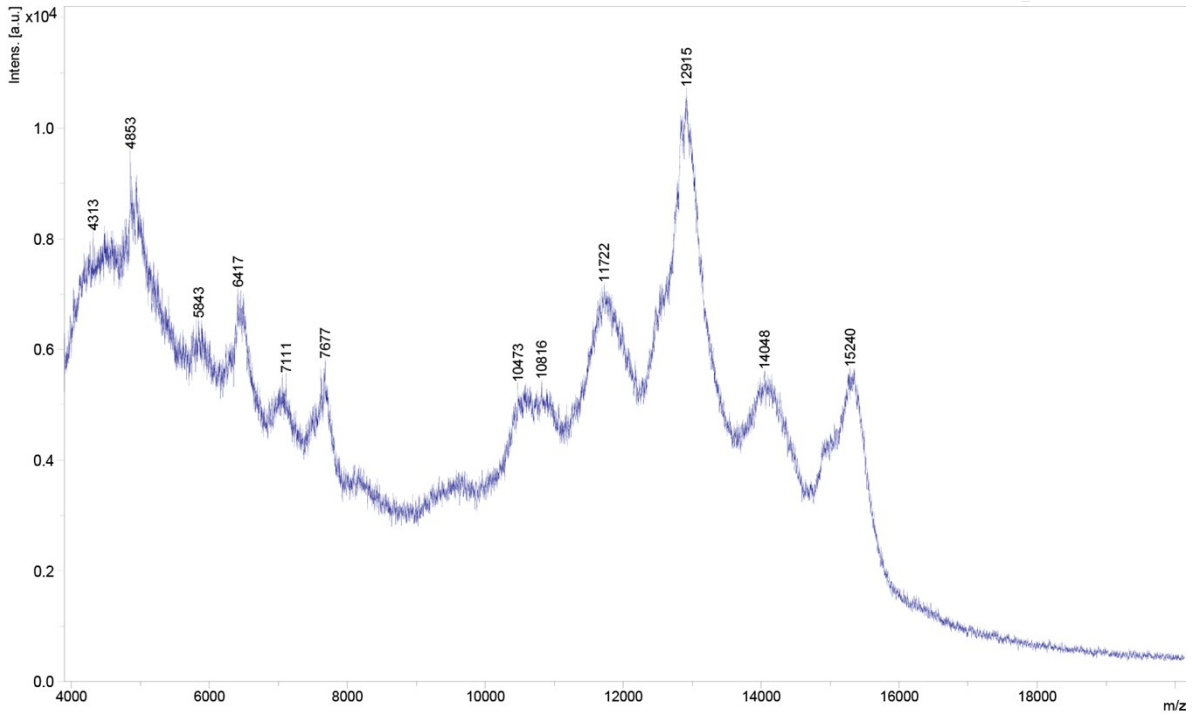




^{1}H NMR spectrum of **3b** (300 MHz, DMSO-d_6) at 298K.



FTIR spectrum of **3b** showing the dissapearance of the signals of alkyne and azide groups present in the synthetic precursors



MS (MALDI-TOF) spectrum of **3b**

Supplementary Figures

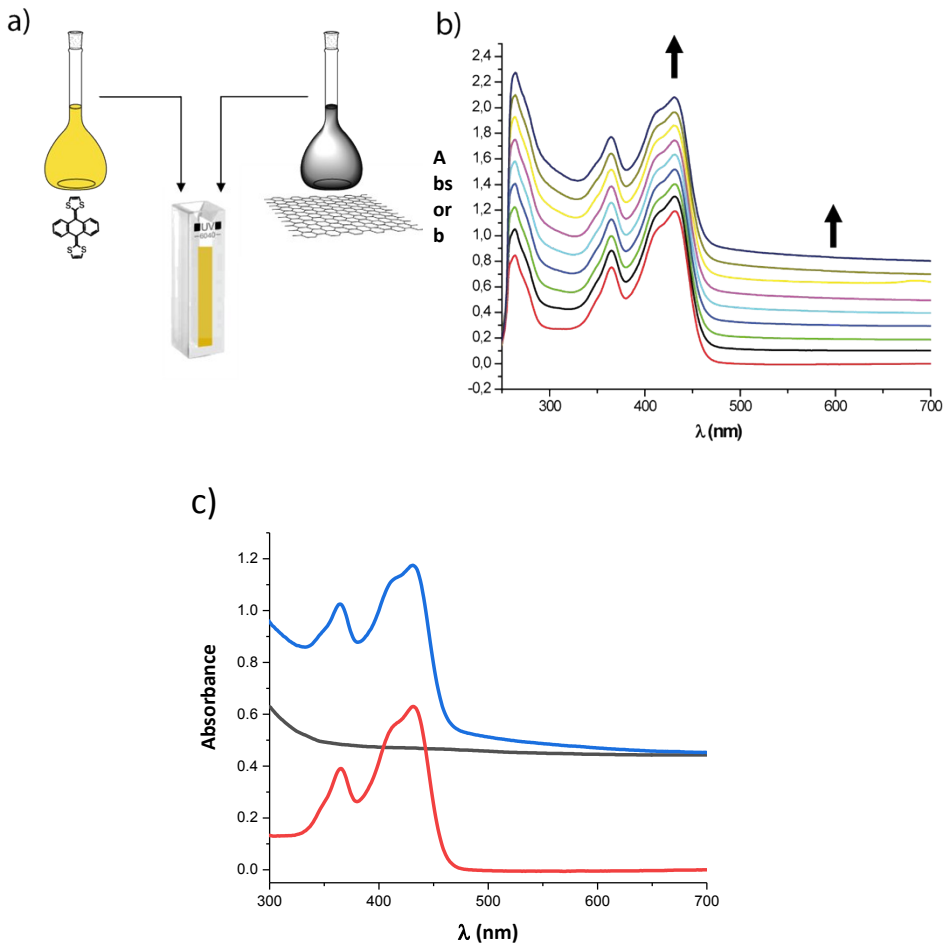


Figure S1: a) Schematic representation of the titration protocol, where increasing amounts of graphene were added to a solution of exTTF of constant concentration ($3.82 \cdot 10^{-5}$ M) and b) UV-vis absorption spectra of the titration for exTTF. Each addition corresponds to 100 µL of the graphene solution. c) UV-vis absorption spectra of FLG (black), exTTF (red) and mixture of both (blue) showing the resulting spectrum as the arithmetic addition of the separated absorption spectra.

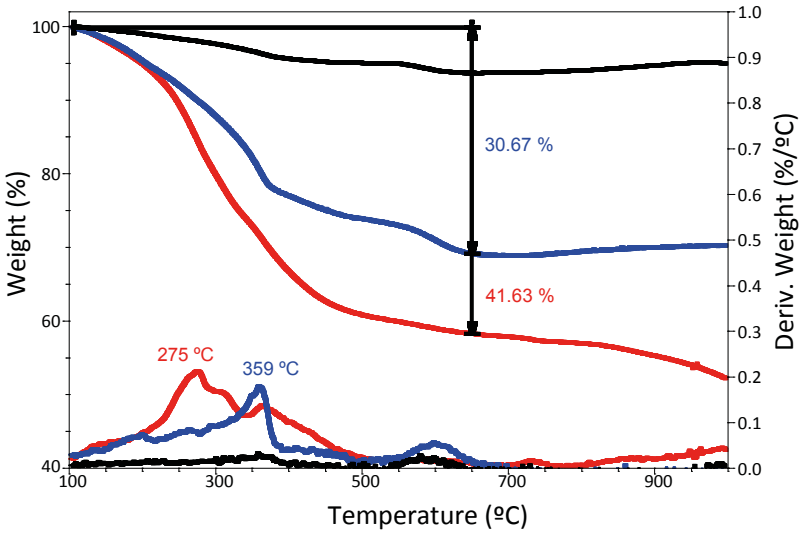


Figure S2: TGA weight loss and first derivative curves under inert conditions of the exfoliated graphene (black) and the supramolecular **FLG-3a** (blue), together with the thermal decomposition of **3a** (red).

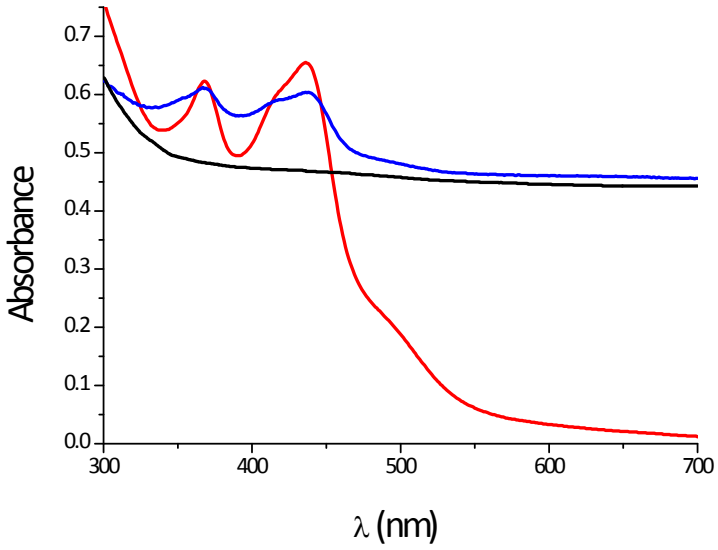


Figure S3: UV-vis spectra of FLG (black), **3a** (red) and **FLG-3a** (blue) in NMP.

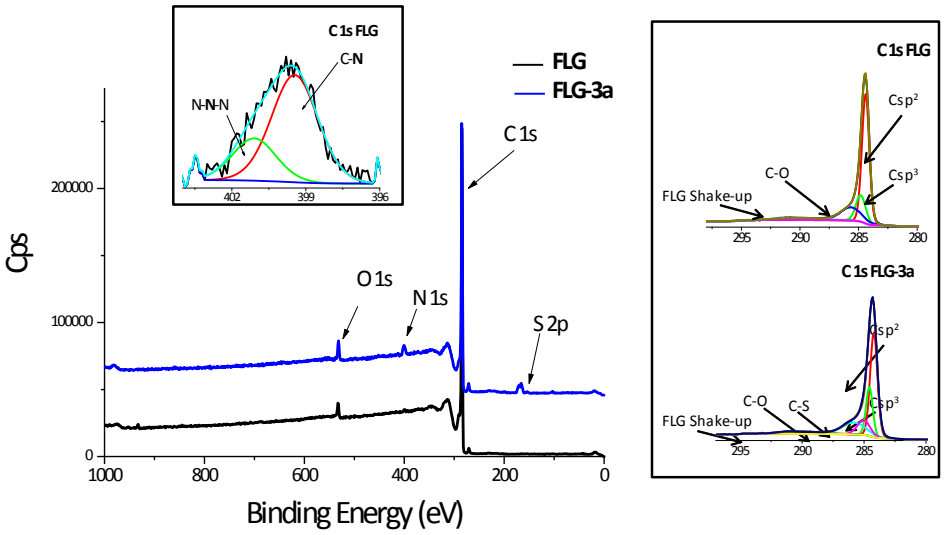


Figure S4: XPS analysis of FLG (black), and the supramolecular graphene aggregate **FLG-3a** (blue). Detailed inset of the carbon band of FLG (upper graph) compared to complex **FLG-3a** (lower graph) and detailed inset of the N 1s band of **FLG-3a**.

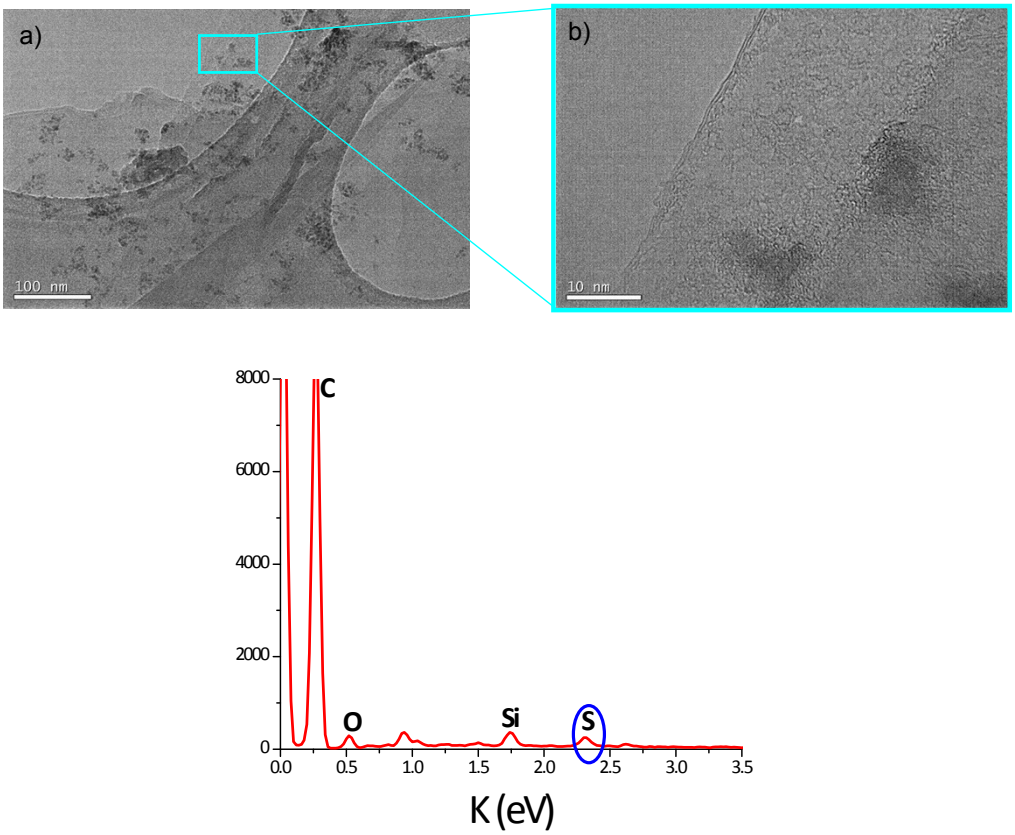


Figure S5: TEM images of a) **FLG-3a** obtained after the exfoliation procedure with **3a** and b) magnification where the graphene layers can be observed (right) together with some round shaped shadows that could be aggregates of **FLG-3a**. The EDX analysis of the aggregate **FLG-3a** is shown at the bottom of the figure highlighting the presence of sulfur.

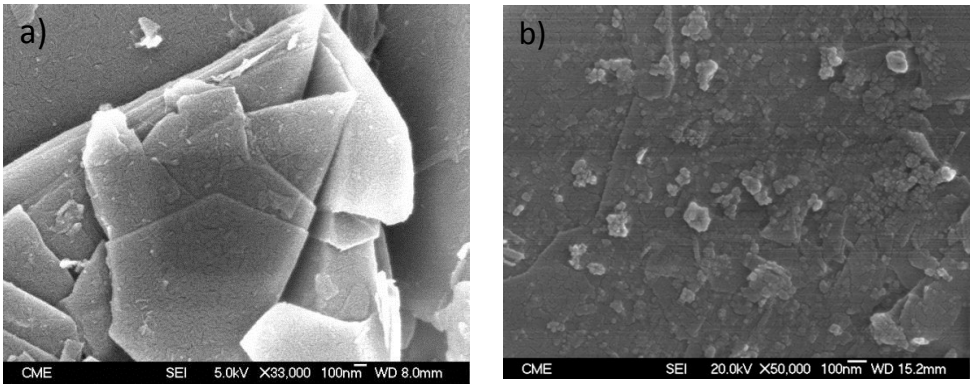


Figure S6: SEM micrographs of a) FLG obtained after the exfoliation procedure with NMP and b) graphene obtained after the exfoliation with a solution of **3a** in NMP; small round shaped agglomerates are visible.