Electronic Supplementary Material (ESI) for RSC Advances.

Understanding the Colorimetric Properties of Quinoxaline-Based Pi-Conjugated Copolymers by Tuning their Acceptor Strength: A Joint Theoretical and Experimental Approach

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1- **Geometry Optimization of trimers**

The HOMO energy is influenced by the nature of the substituents, the dihedral angles along the chain, and the polarization effect in the solid state. Due to the generally very weak inter-ring twisting potentials, the difference between the gas phase- and solid state dihedral angles is expected to increase with the increasing dihedral angles across the series (Table S1). Accordingly, the decrease in the IP values resulting from the geometry flattening in solid films is expected to increase across the series. This effect is thus opposite to the increasing IP values predicted on the bases of the increasing electronegativity (hence decreasing HOMO energies) across the series, thus giving a possible explanation for the dichotomy between the theoretical and the experimental trends. The above argument seems to be comforted by the global agreement between the evolution of the theoretical LUMO energies and the trend of the EA^{SS} values (globally increasing by 0.20 eV across the series of polymers, Figure S1). The LUMOs are almost exclusively concentrated on the quinoxaline rings, suggesting that the decreasing LUMO energies cannot depend on the D-A dihedral angle but only on the nature of the substituent.

	D_1A_2	A2D3	D3D4	D4A5	A5D6	D6D7	D7A8	A8D9
trim3-OMe_{para}	2.6	22.5	6.6	23.7	23.7	6.6	21,9	2.6
trim3-OMe_{meta}	-2.2	21.0	3.6	20.7	20.6	3.6	21.1	-1.7
trim3-H	-2.4	20.5	4.0	21.3	21.3	4.0	20.5	-2.4
trim3-F	-0.2	21.4	8.9	21.9	21.9	8.9	21.4	-0.2
trim3-COOMe	-3.7	21.3	6.7	23.5	23.5	7.0	22.0	4.7
trim3-CN	-1.4	25.6	6.0	27.6	27.6	6.0	25.6	-1.4

Table S1: Dihedral angles for optimized trimer structures (angles in °). The dihedral angles corresponding by symmetry are highlighted.

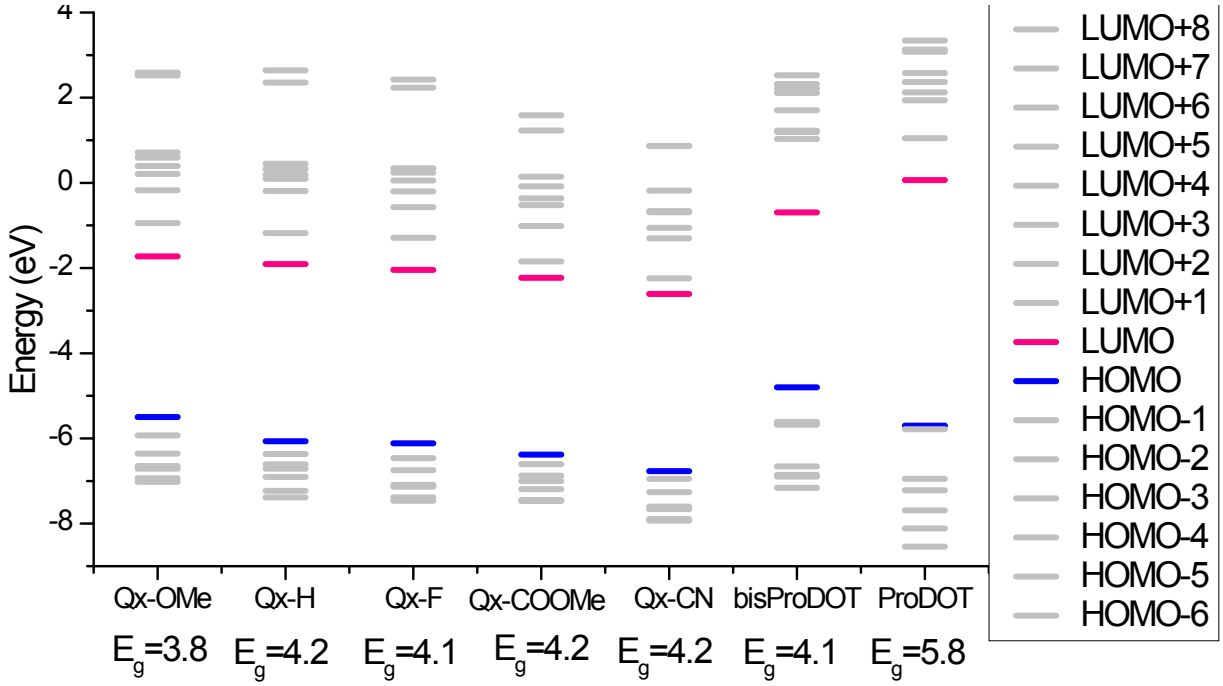


Figure S1: Evolution of the HOMO-6 to LUMO+8 energy levels corresponding to prodot , di-prodot, and the substituted quinoxaline compounds (B3LYP/6-31G(d,p) level in "gas phase"). The relative HOMO-LUMO energy gaps as compared to the nonsubstituted compound are also indicated (ΔE_g). All values ate in eV.

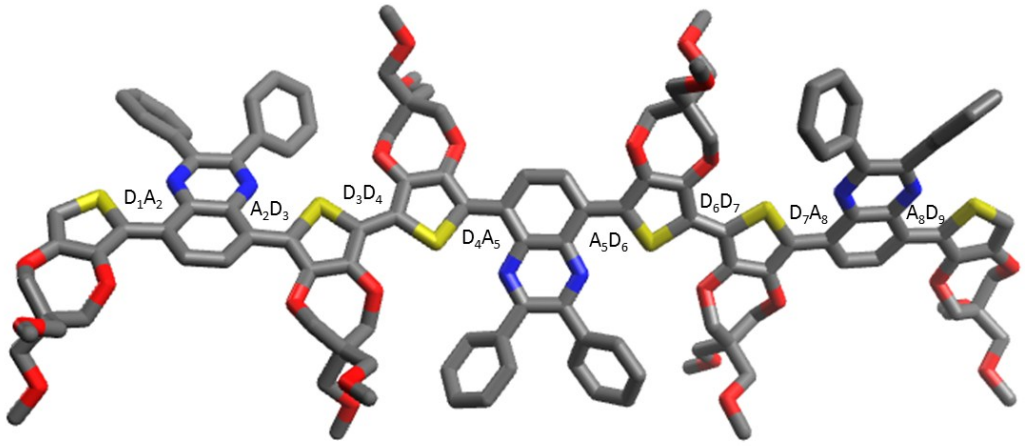
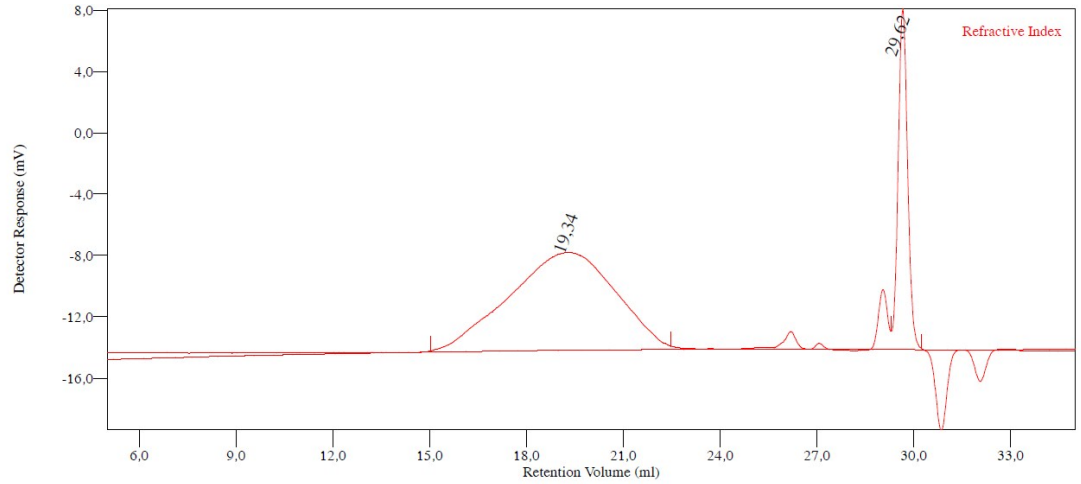


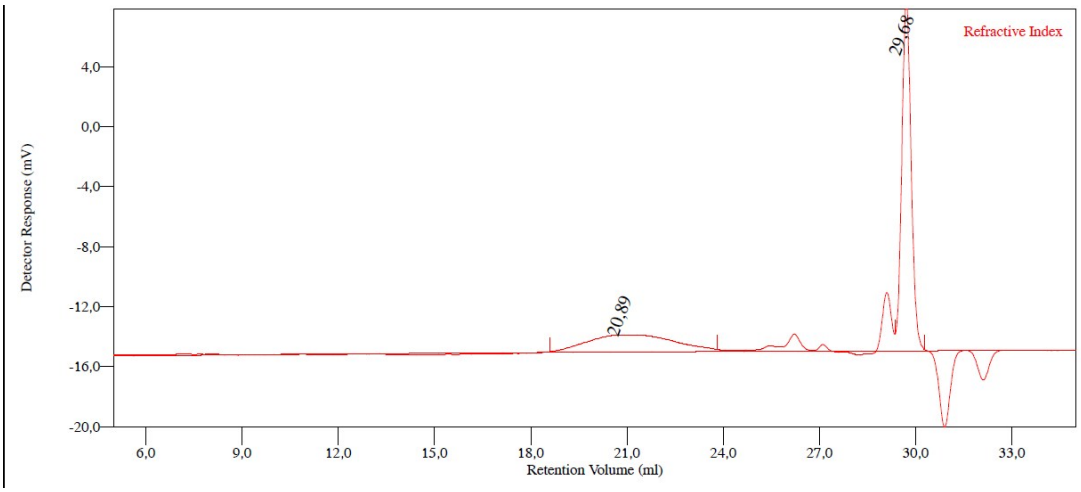
Figure S2 : Identification of the dihedral angles along the polymer chain

2- **SEC DATA**

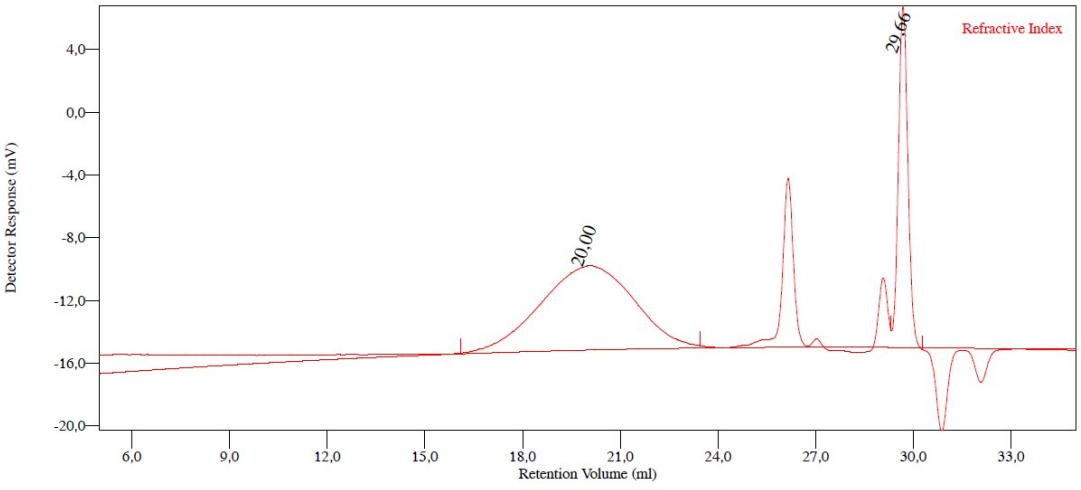
P3-H



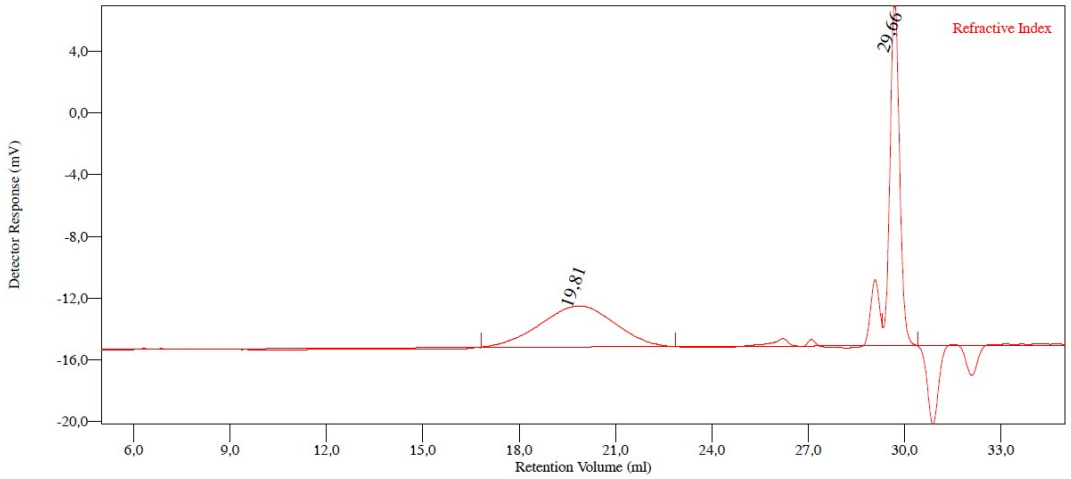
P3-OMe



P3-F



P3-COOMe



P3-CN

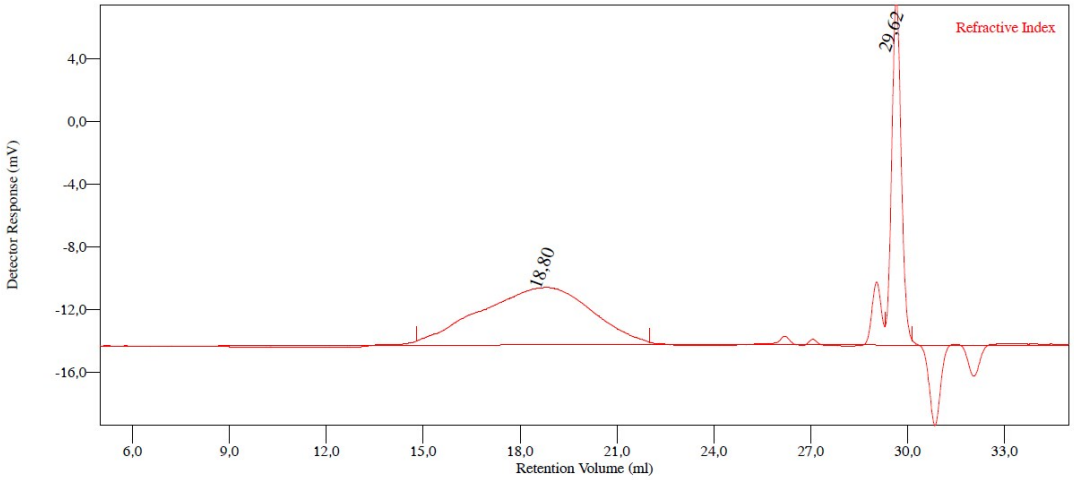


Figure S3 : GPC chromatogram

References :

(1) Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. *Nat Mater,* **2008**, *7*, 795.

(2) Li, J.-C.; Kim, S.-J.; Lee, S.-H.; Lee, Y.-S.; Zong, K.; Yu, S.-C. *Macromolecular Research,* **2009**, *17*, 356.

(3) Miao, Q.; Gao, J.; Wang, Z.; Yu, H.; Luo, Y.; Ma, T. *Inorganica Chimica Acta,* **2011**, *376*, 619.