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New Journal of Chemistry

Electronic Supplementary Information (ESI):

Aggregation phenomena in photobicyclised pyridinium salts

A. Aracena*[a], M. C. Rezende *[b], M.V. Encinas *[b], C. Vergara[b] and S. O. Vásquez[a].

NMR spectra of studied compounds:

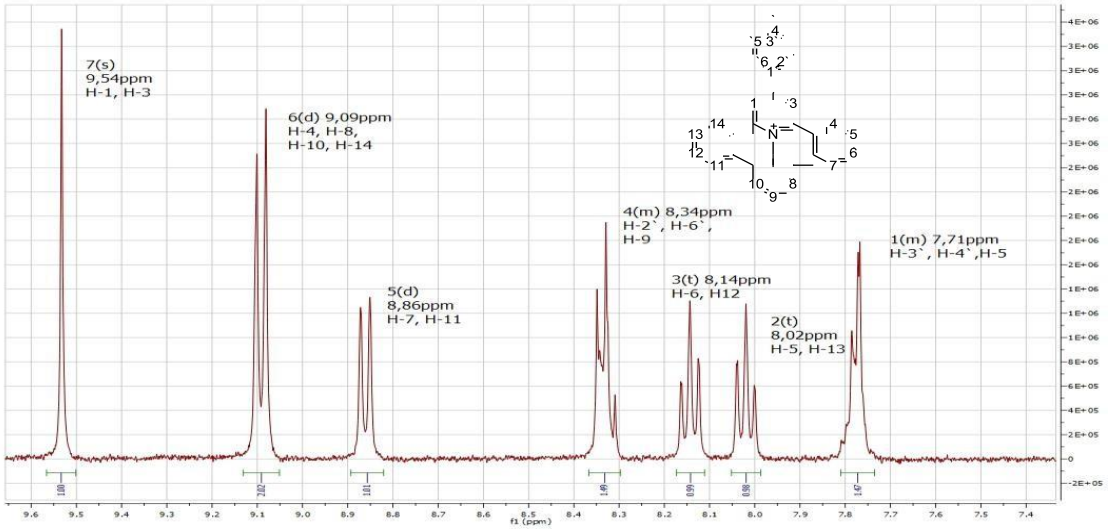

Figure 1 - ^{1}H NMR spectrum of the 2-phenylbenzo[8,9]quinolizino[4,5,6,7-fed]phenanthridinylium tetrafluoroborate ($PQPBF_4$) in $(CD_3)_2CO$.

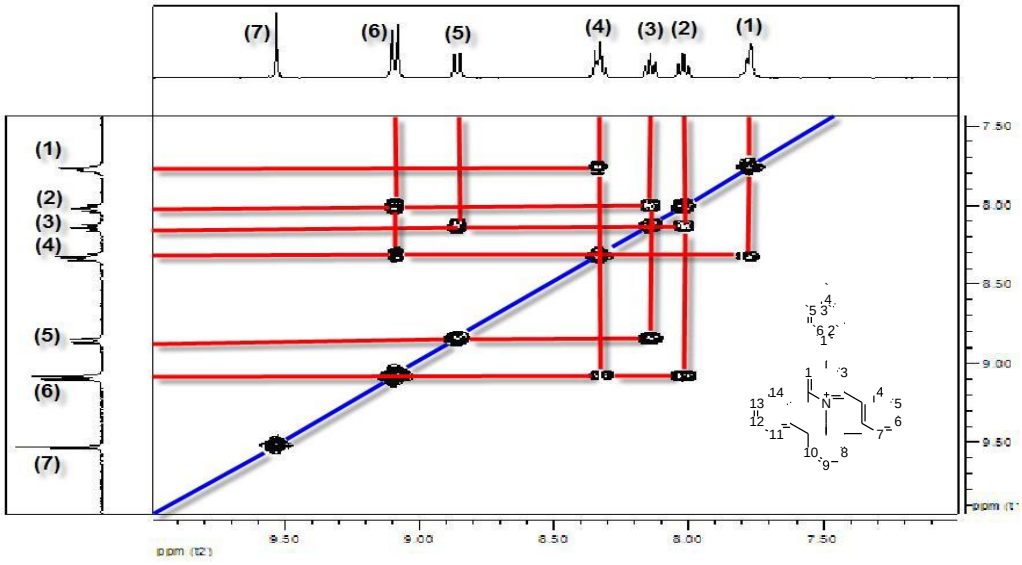

Figure 2 – 2-D ^{1}H-^{1}H COSY plot of the 2-phenylbenzo[8,9]quinolizino[4,5,6,7-fed]phenanthridinylium tetrafluoroborate ($PQPBF_4$) in $(CD_3)_2CO$

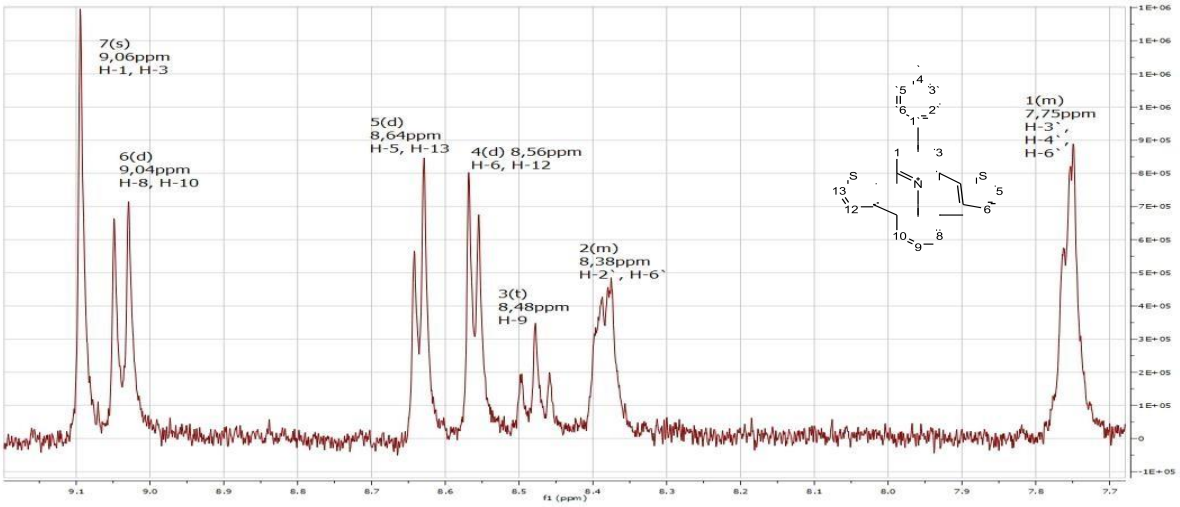

Figure 3 - ^{1}H NMR spectrum of the 2-phenylbenzo[ij]pyrido[2,1,6-de]dithieno[3,2-b:2',3'-g] quinolizin-13-ium perchlorate (BPDTQClO_4) in $(CD_3)_2CO$

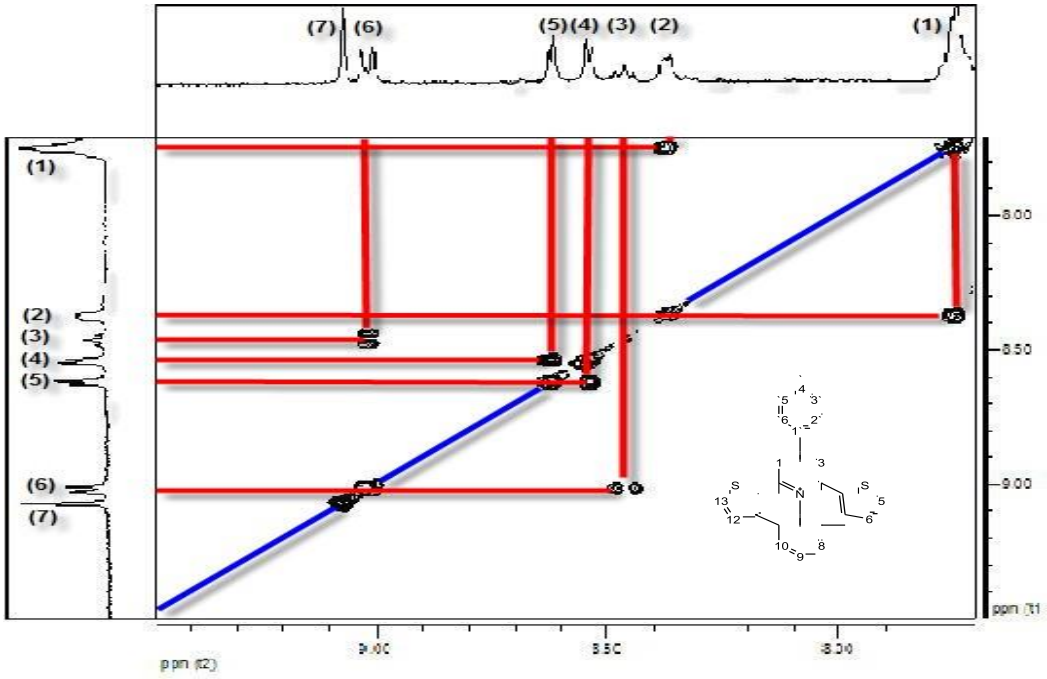

Figure 4 – 2-D ^{1}H-^{1}H COSY plot of the 2-phenylbenzo[ij]pyrido[2,1,6-de]dithieno[3,2-b:2',3'-g] quinolizin-13-ium perchlorate (BPDTQClO_4) in $(CD_3)_2CO$

Structures and total energies of cationic dimers of PQP^+ and $BPDTQ^+$:

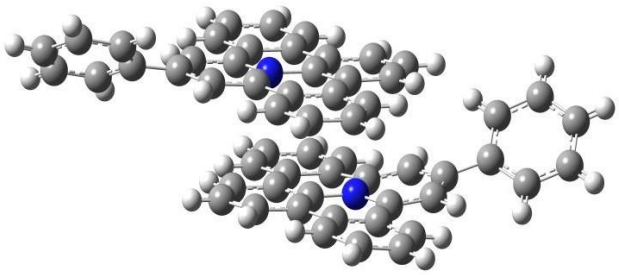

Figure 5 – Structure of the cationic dimer of PQP^+ in the parallel conformation, obtained from x-ray measurements (D. Wu, W. Pisula, V. Enkelmann, X. Feng, K. Müllen, *J. Am. Chem. Soc.*, 2009, **131**, 9620. ja902420u si 002.cif). Single-point calculation employing a DFT PBE0/6-31G(d) method, and the PCM model to mimic the aqueous medium yielded a total energy of -2337.89377692 hartrees, corresponding to -1467049.4 $kcal.mol^{-1}$.

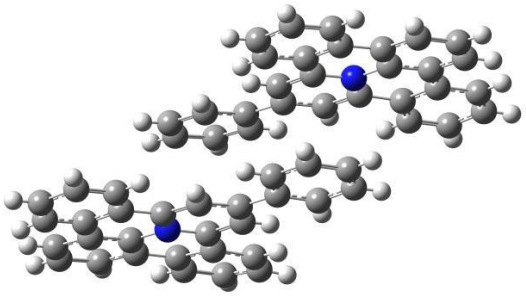

Figure 6 - Structure of the cationic dimer of PQP^+ in the antiparallel conformation, obtained from x-ray measurements (D. Wu, W. Pisula, V. Enkelmann, X. Feng, K. Müllen, *J. Am. Chem. Soc.*, 2009, **131**, 9620. ja902420u si 003.cif). Single-point calculation employing a DFT PBE0/6-31G(d) method, and the PCM model to mimic the aqueous medium yielded a total energy of -2337.90080034 hartrees, corresponding to – 1467053.8 $kcal.mol^{-1}$.

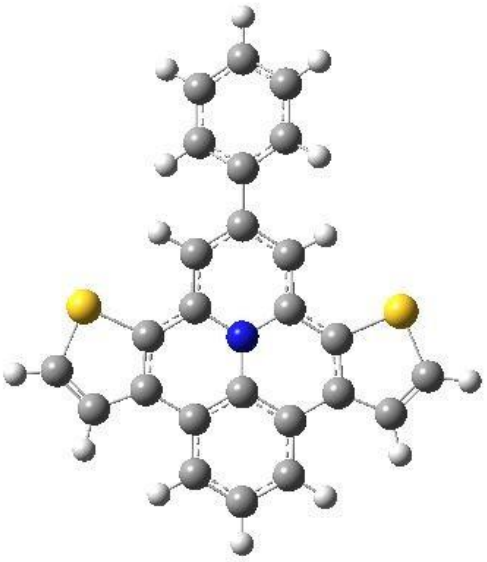

Figure 7 – Structure of the monomeric cation of $BPDTQ^{+}$, optimized in the gas phase with the DFT B3LYP/6-31G(d) method, with a total energy of -1812.06359 hartrees.

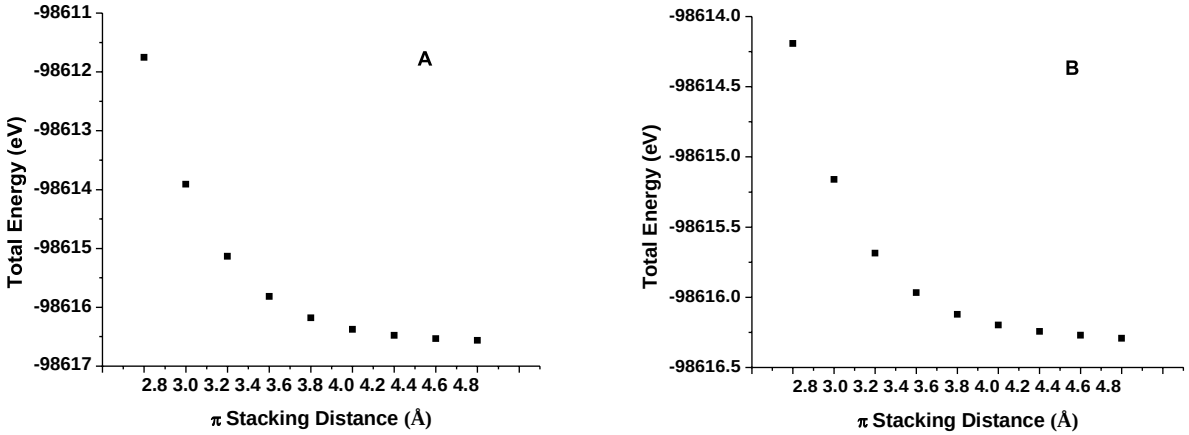

Figure 8 – Variation of the calculated heat of formation of the antiparallel (A) and parallel (B) $BPDTQ^{+}$ dimer, as a function of the distance between the two monomeric units. Total energies were obtained from single-point calculations employing the optimized structure of the monomer of Figure 7, and varying the distance between the two monomeric units.

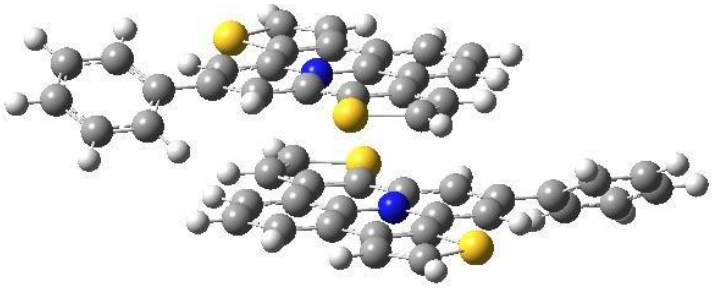

Figure 9 - Structure of the cationic dimer of $BPDTQ^{+}$ in the parallel conformation, with a distance between the two parallel rings of 4 Å. Single-point calculation employing a DFT PBE0/6-31G(d) method, and the PCM model to mimic the aqueous medium yielded a total energy of -3621.28232801 hartrees, corresponding to – 2272387.3 $kcal.mol^{-1}$.

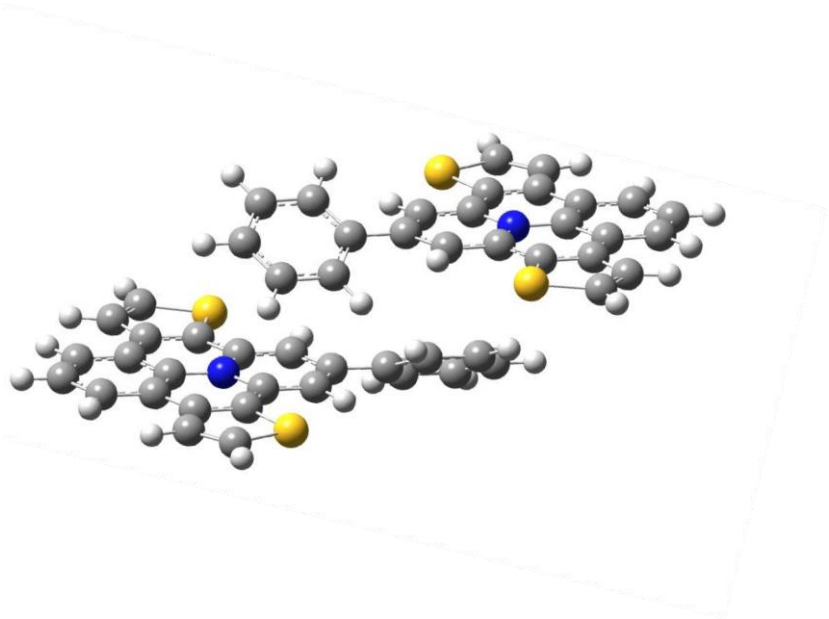

Figure 10 - Structure of the cationic dimer of $BPDTQ^{+}$ in the antiparallel conformation, with a distance between the two parallel rings of 4 Å. Single-point calculation employing a DFT PBE0/6-31G(d) method, and the PCM model to mimic the aqueous medium yielded a total energy of -3621.27731597 hartrees, corresponding to – 2272384.1 $kcal.mol^{-1}$.