

Photo-induced Charge Transfer in Azapyrene-Tetrathiafulvalene TriadsP. Zhou¹, U. Aschauer¹, T. Feurer², R. Häner¹, S. Liu^{1*}

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Tetrathiafulvalene (TTF)-based donor-acceptor (D-A) ensembles have attracted a lot of attention due to their unique (opto)electronic properties and potential applications in organic semiconductors, photovoltaics, sensors, switches and molecular electronics.¹⁻³ To develop high-performance electronic devices, control over multiple charge-transfer (CT) pathways in D-A ensembles is of prime importance. Recently, we have demonstrated chemical and ultrafast optical regulation of distinct photo-induced charge flows within such D-A systems.^{4,5} As a continuation of our ongoing work, we herein describe redox and optical properties of new D-A ensembles (Chart 1) which were prepared by covalent linkage of two TTF donor units to a central azapyrene acceptor either with or without two tert-butyl groups. A detailed experimental and theoretical study of electronic interactions between D and A units and ICT processes in these triads is presented.

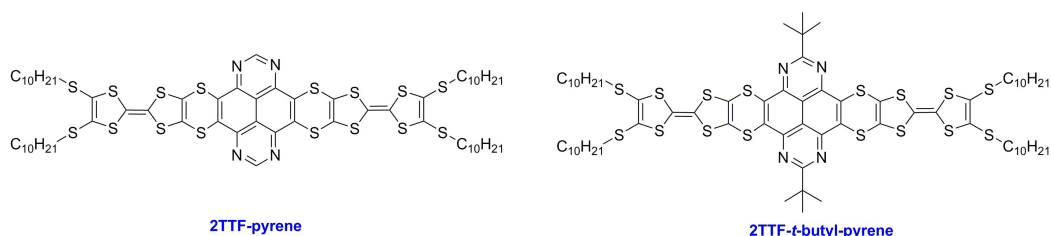


Chart 1. Chemical structures of triads 2TTF-pyrene and 2TTF-t-butyl-pyrene.

- [1] Bergkamp, J. J.; Decurtins, S.; Liu, S. X., Current advances in fused tetrathiafulvalene donor-acceptor systems. *Chem. Soc. Rev.* **2015**, *44*, 863-74.
- [2] Jana, A.; Ishida, M.; Park, J. S.; Bähring, S.; Jeppesen, J. O.; Sessler, J. L., Tetrathiafulvalene-(TTF-) Derived Oligopyrrolic Macrocycles. *Chem. Rev.* **2017**, *117*, 2641-2710.
- [3] Pfattner, R.; Pavlica, E.; Jaggi, M.; Liu, S.-X.; Decurtins, S.; Bratina, G.; Veciana, J.; Mas-Torrent, M.; Rovira, C., Photo-induced intramolecular charge transfer in an ambipolar field-effect transistor based on a π -conjugated donor-acceptor dyad. *J. Mater. Chem. C* **2013**, *1*, 3985-3988.
- [4] Zhou, P.; Aschauer, U.; Decurtins, S.; Feurer, T.; Häner, R.; Liu, S. X. Chemical control of photoinduced charge-transfer direction in a tetrathiafulvalene-fused dipyrrolylquinoxaline difluoroborate dyad. *Chem. Commun.* **2020**, *56*, 13421-13424.
- [5] Rohwer, E. J.; Geng, Y.; Akbarimoosavi, M.; Daku, L. M. L.; Aleveque, O.; Levillain, E.; Hauser, J.; Cannizzo, A.; Häner, R.; Decurtins, S.; Stanley, R. J.; Feurer, T.; Liu, S. X. Optically Controlled Electron Transfer in a Re(I) Complex. *Chem. Eur. J.* **2021**, *27*, 5399-5403.