

Motivation

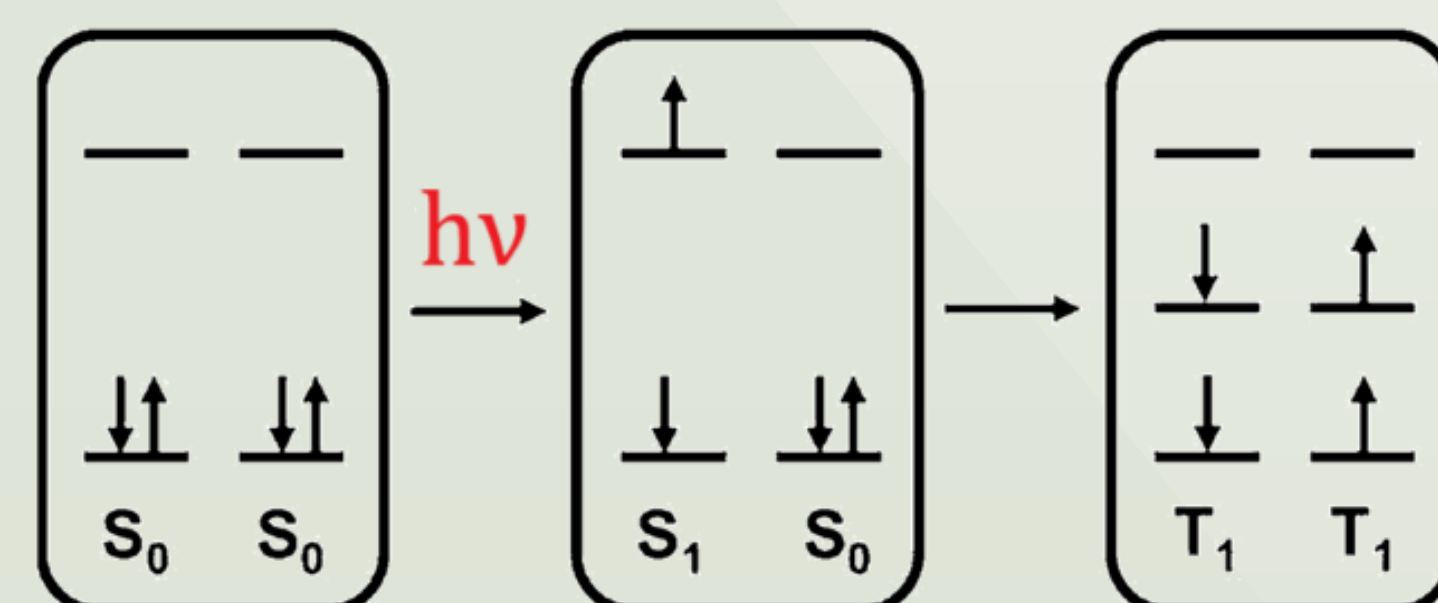
Thermalization accounts for most of the energy losses in photovoltaic devices, limiting the efficiency up to only 32%—Shockley-Queisser limit. Overcoming this is imperative for higher photovoltaic efficiency.

Multi-Exciton Generation processes such as **Singlet Fission (SF)** could be one of the solutions

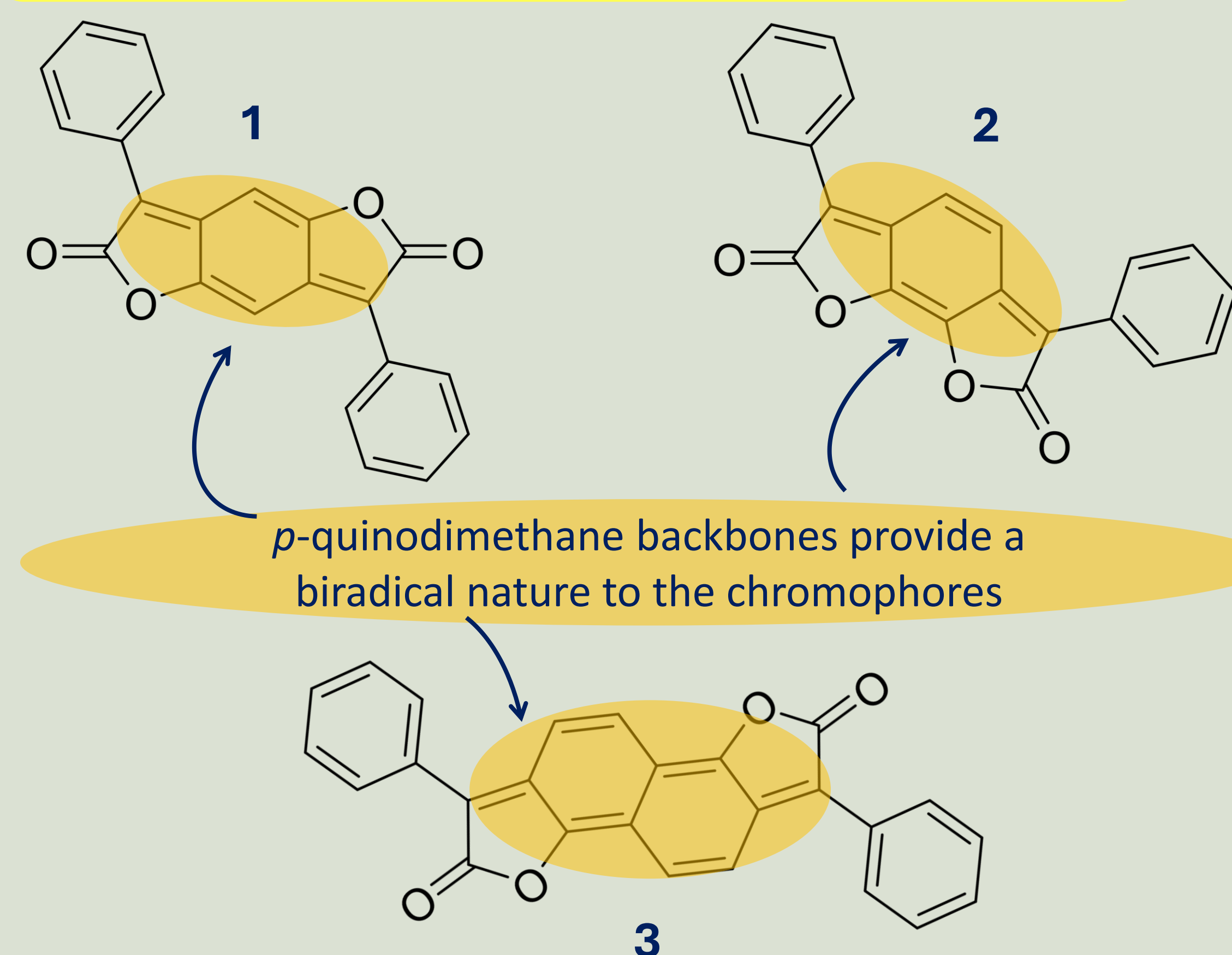
An ultrafast process where a photoexcited singlet state (S_1) splits into two lower-energy triplet states (T_1) via interaction with a neighboring ground-state chromophore

But!

$E(S_1) \geq 2E(T_1)$ —The strict energetic requirement, is rarely achieved in common chromophores



Biradicaloid chromophores can be easily tuned to meet this requirement



Observations

SF Energetics

Excited-states energies (in eV) computed using CAM-B3LYP/6-31+G* theory level

Compd	Excited States	Vertical excitation	Adiabatic excitation	0-0 excitation
1	S_1	2.99	2.63	2.56
	T_1	1.20	0.96	0.91
	T_2	2.34	1.97	1.93
2	S_1	2.93	2.50	2.43
	T_1	1.11	0.88	0.83
	T_2	2.43	2.04	1.99
3	S_1	2.61	2.45	2.38
	T_1	0.61	0.48	0.43
	T_2	1.95	1.79	1.73

All three chromophores fulfill the SF energetic criteria

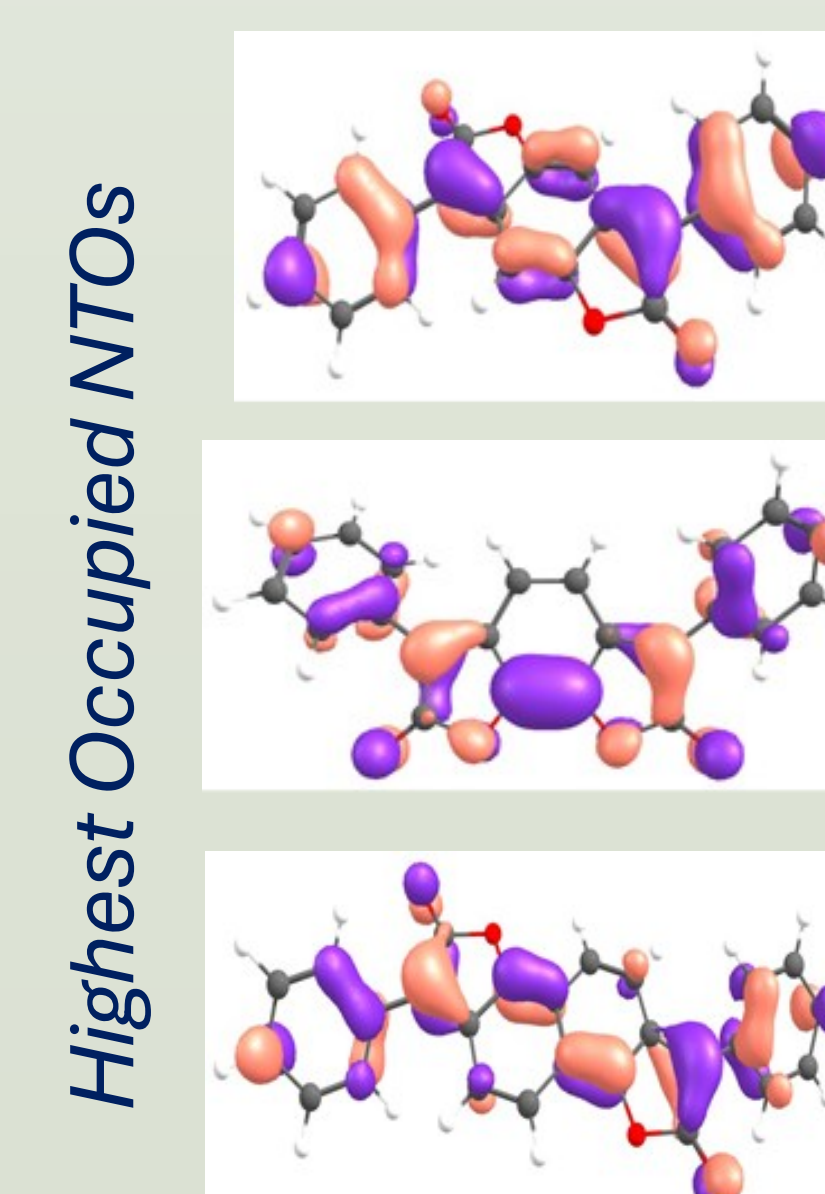
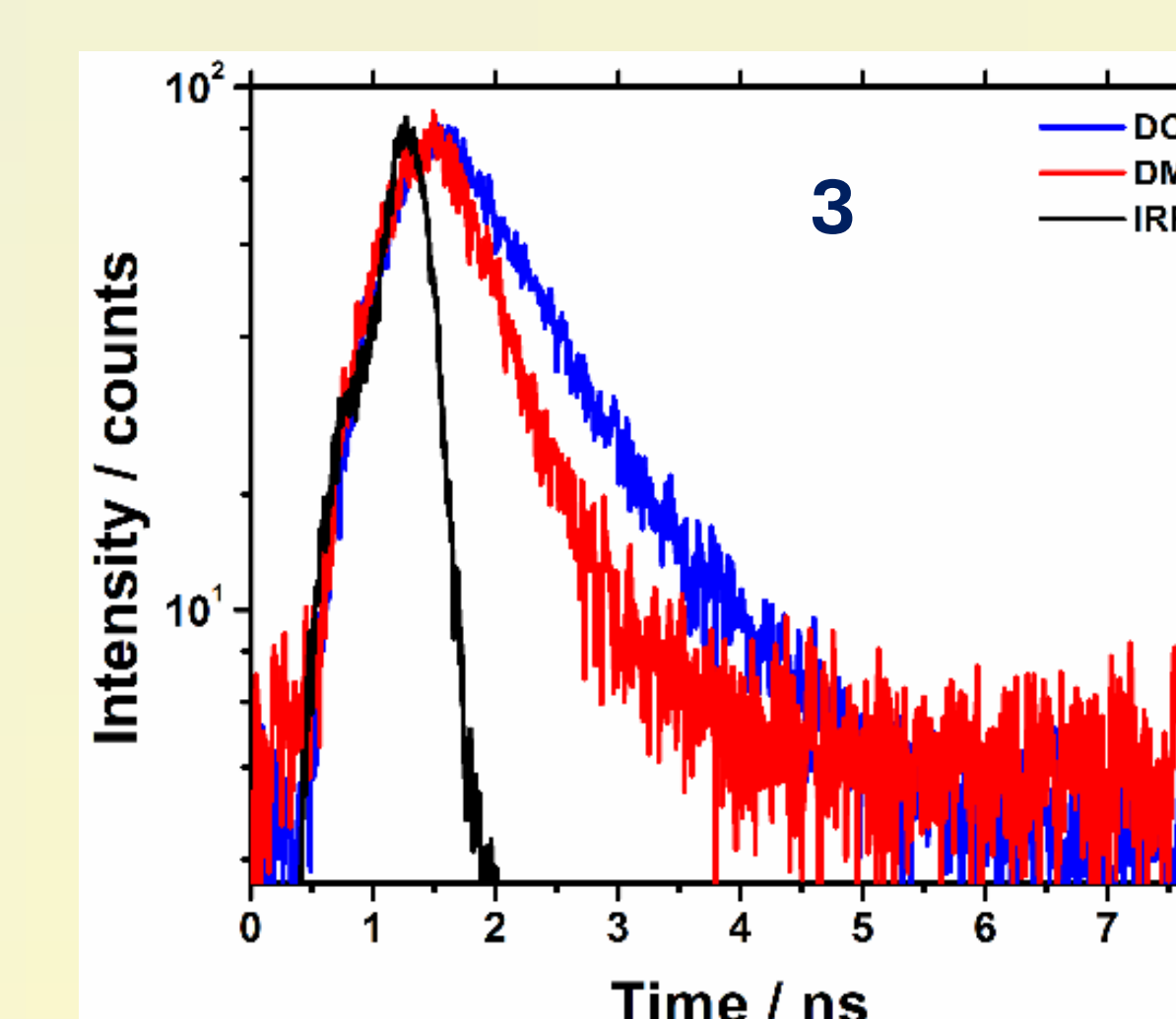
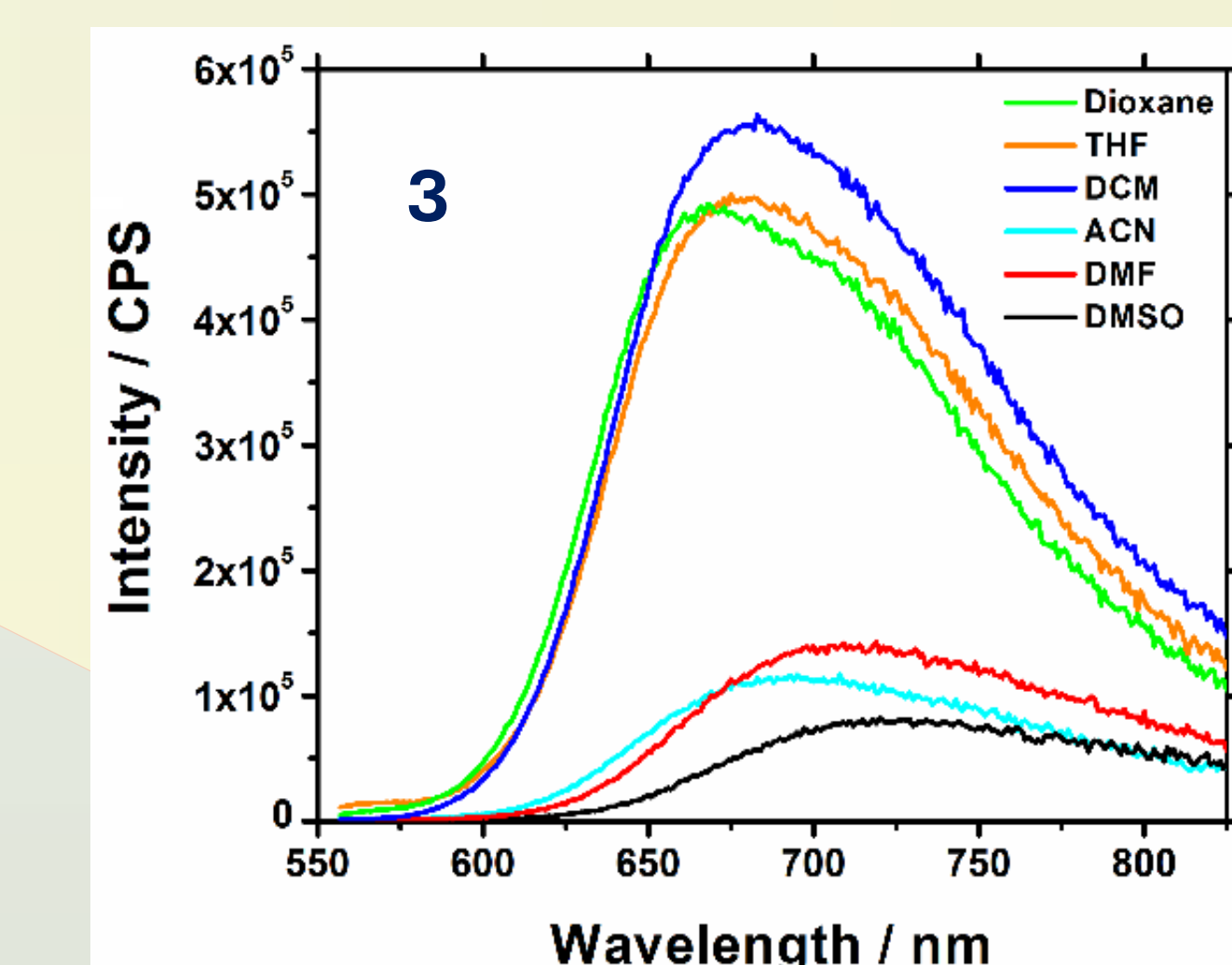
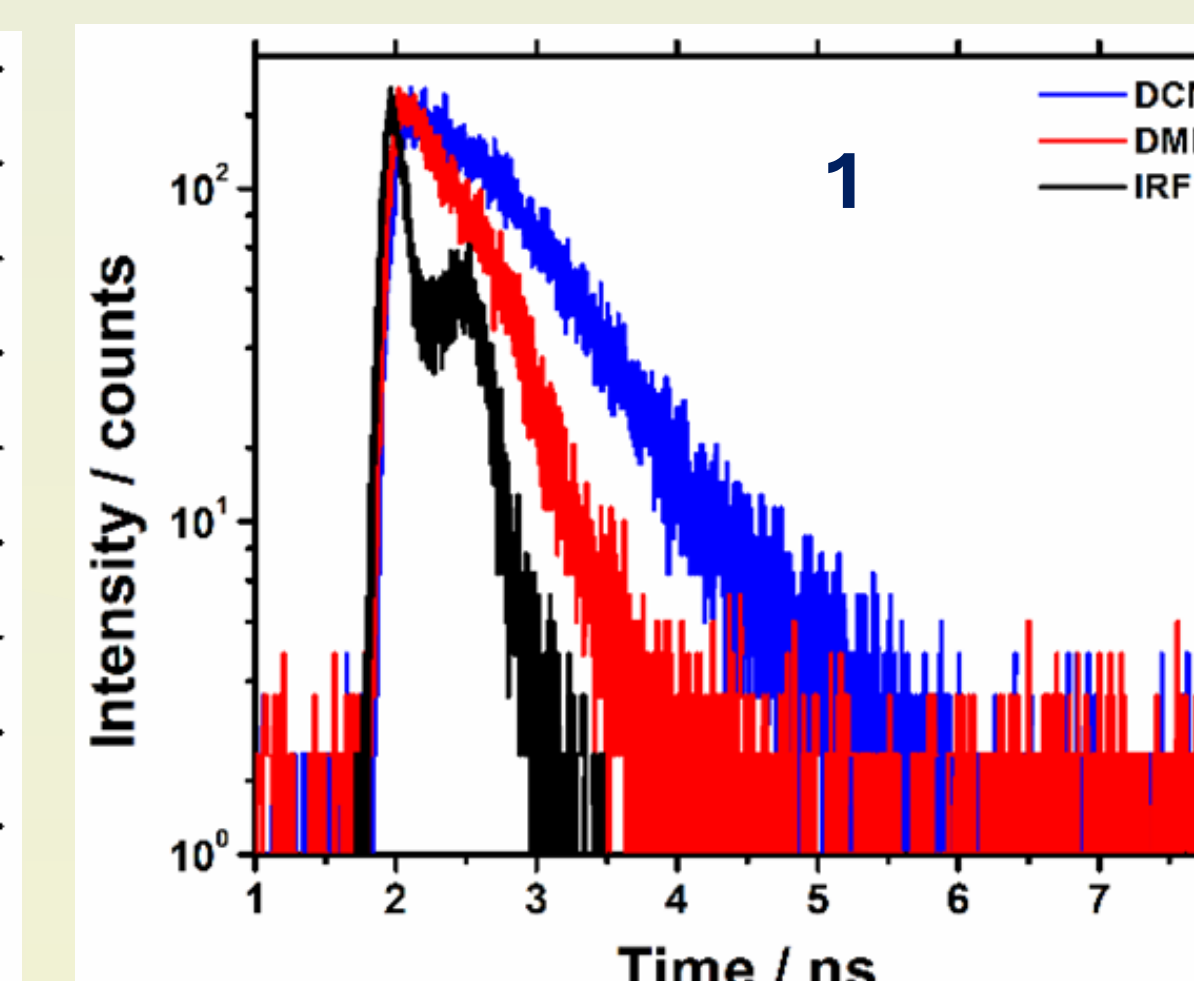
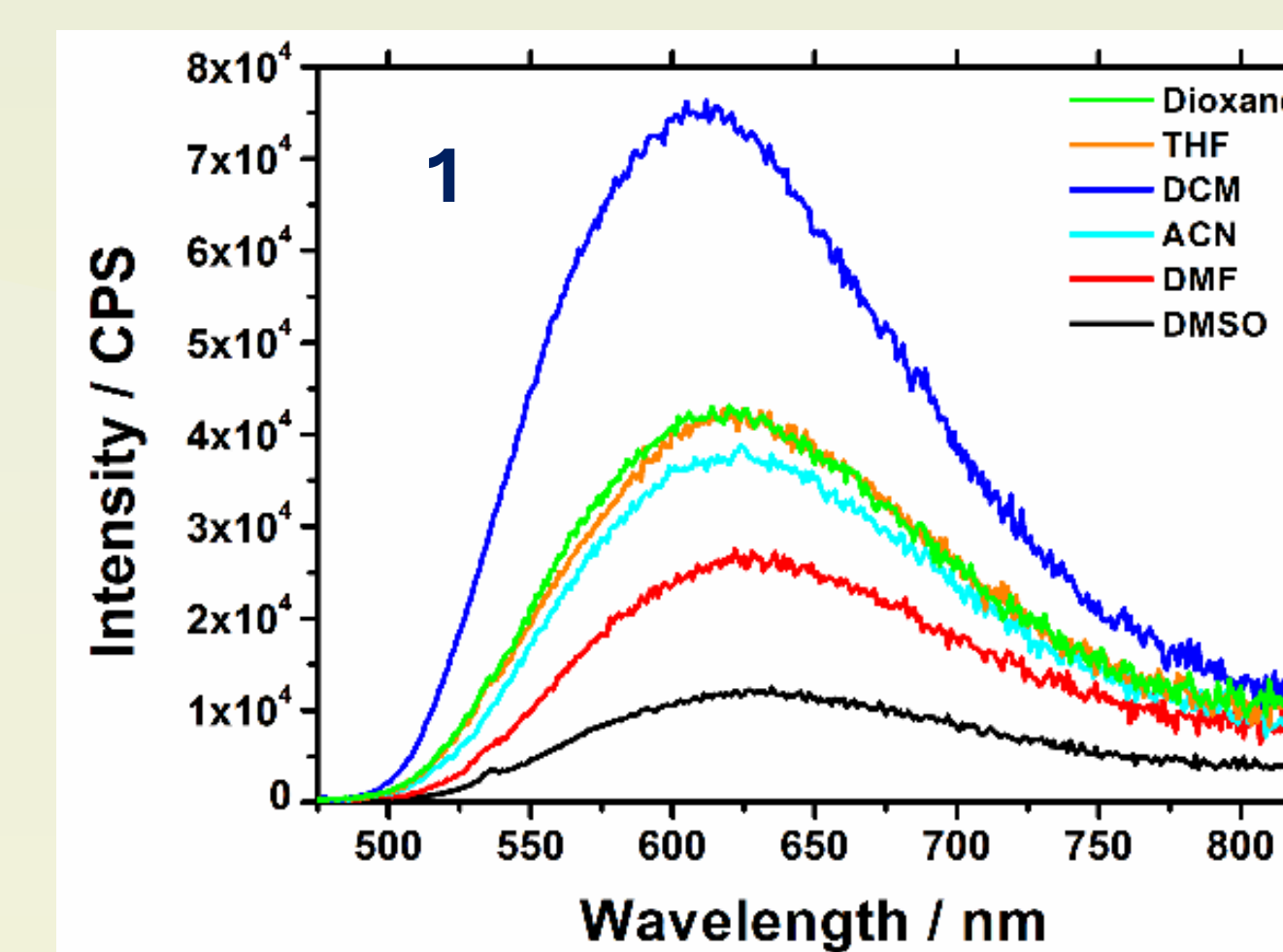
Photophysics

Measurements were carried out in DCM and DMF
Values within parentheses are for DMF

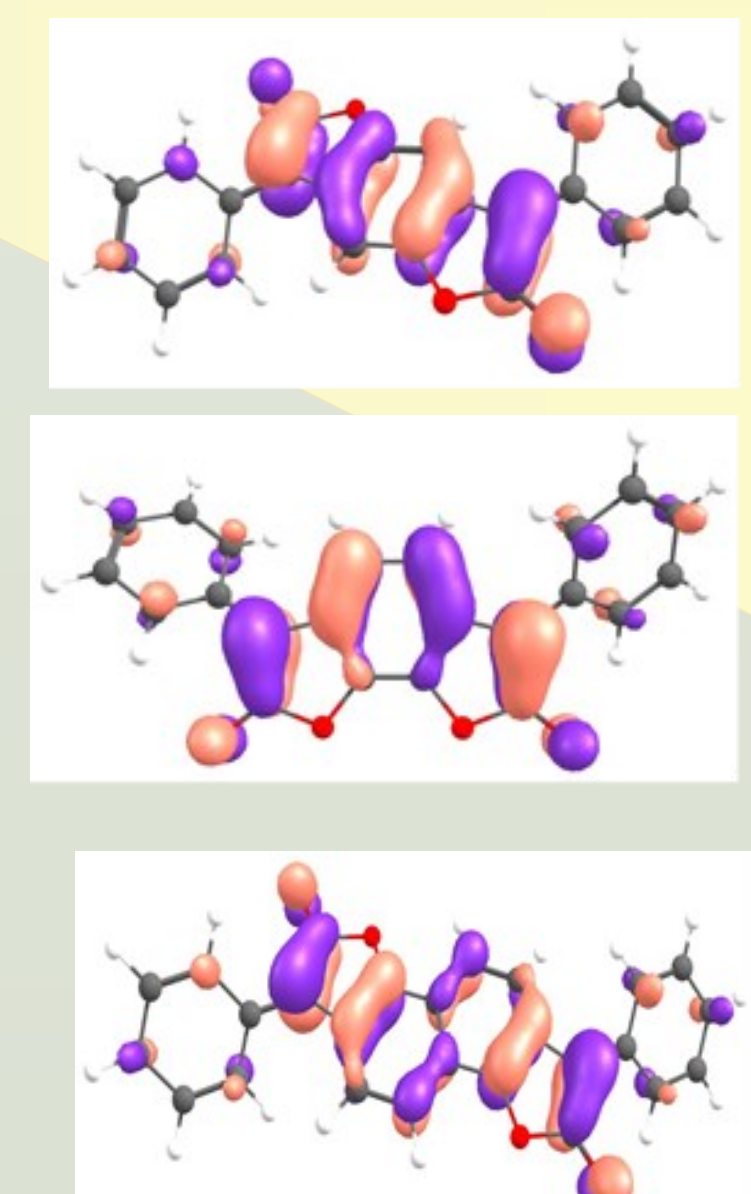
compd	λ_{max}^{ab} / nm	ϵ / $M^{-1}cm^{-1}$	λ_{max}^{fl} / nm	Φ_{fl} / %	τ_{fl} / ns	$k_r \times 10^{-6} / s^{-1}$	$k_{nr} \times 10^{-9} / s^{-1}$
1	472 (467)	50300 (49000)	612 (628)	0.44 (0.13)	0.64 (0.37)	6.89 (3.53)	1.56 (2.71)
2	471 (472)	27700 (44000)	Non-fluorescent				
3	550 (553)	58000 (53000)	684 (709)	2.90 (1.81)	1.06 (0.55)	27.4 (32.8)	0.92 (1.79)

- I. Bathochromic shifts in high-polar DMF
- II. Quenching of emission in high-polar DMF
- III. Non-radiative rates increases in DMF

Such solvent dependence of the emission properties of the chromophores can be attributed to the presence of **Photoinduced Intramolecular Charge Transfer (PICT)** process



Highest Occupied NTOs

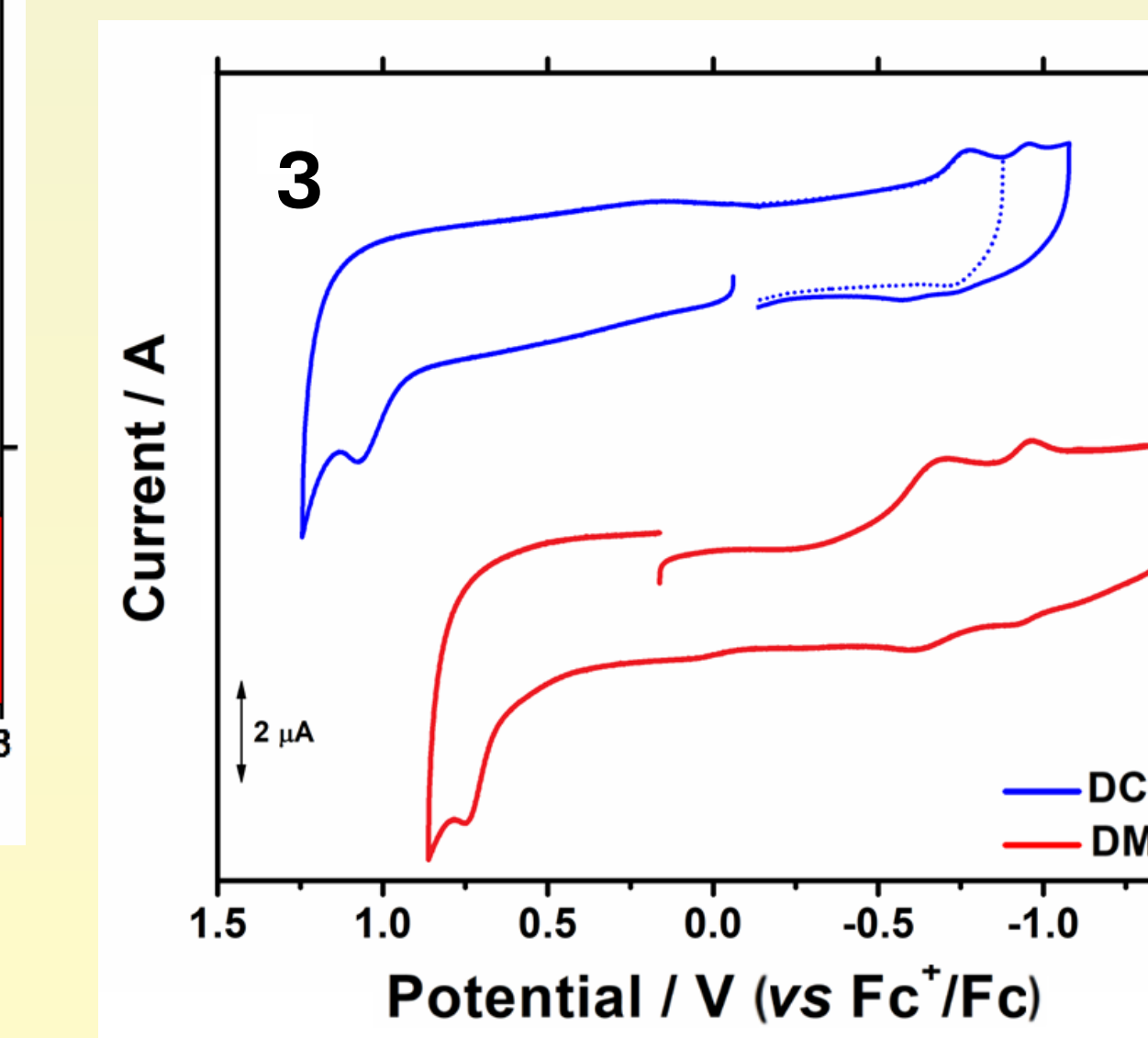
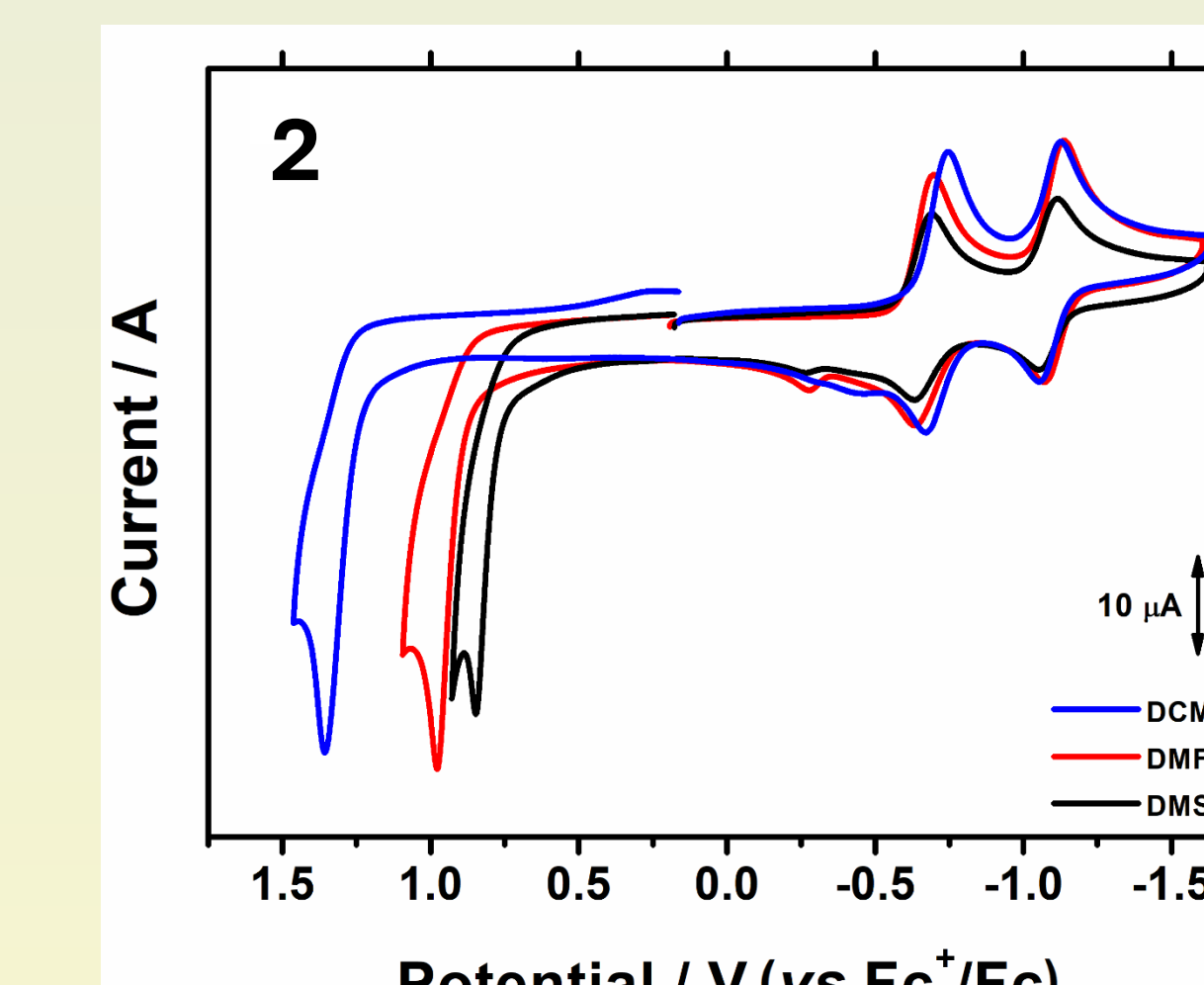
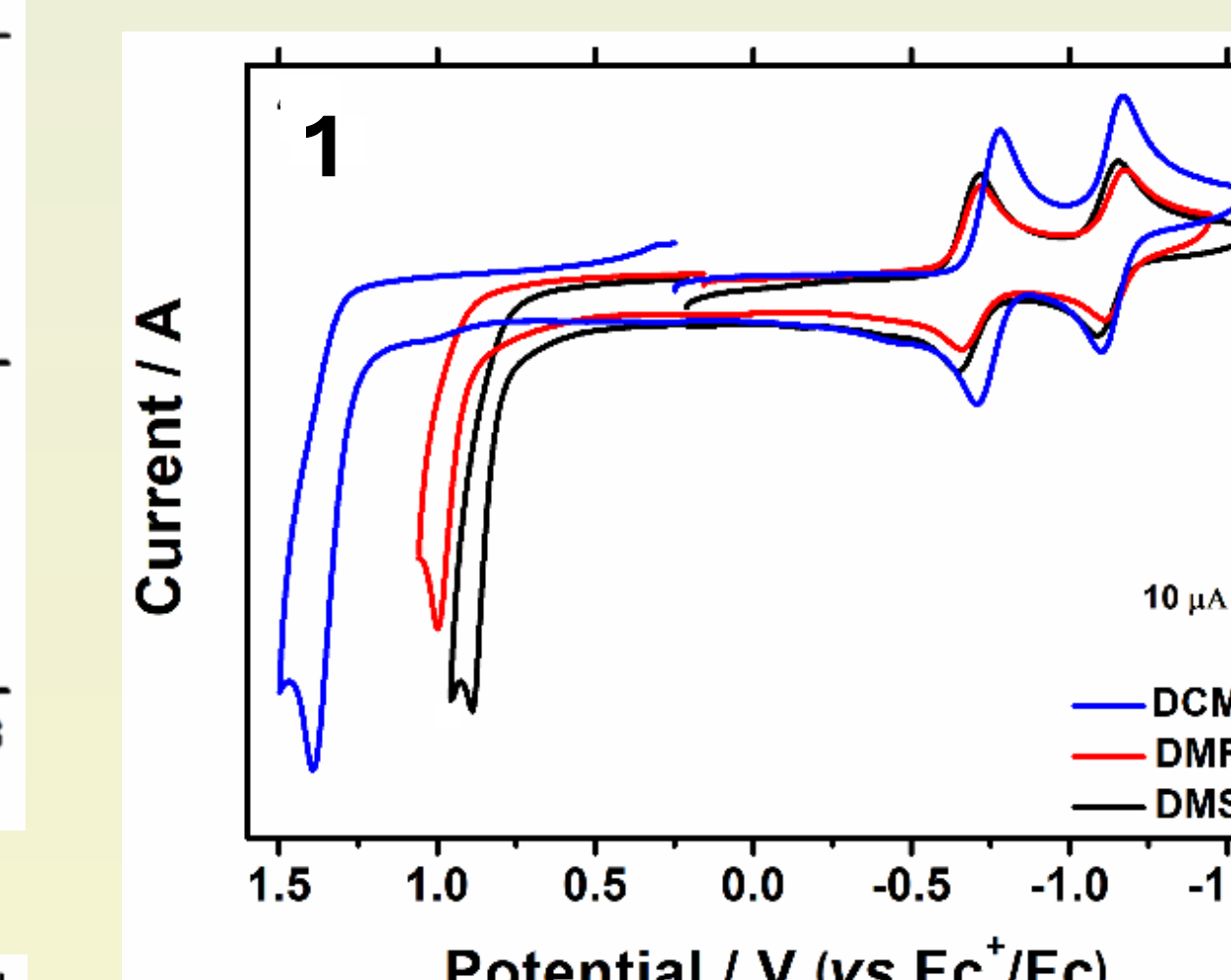


Lowest Unoccupied NTOs

Natural transition orbital (NTO) calculations reveal the presence of **PICT**

- I. Flanking phenyls—**Donors**
- II. Central difuranone cores—**Acceptors**

Cyclic Voltammetry



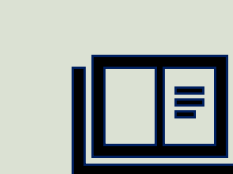
- Redox potential variation with solvent polarity arises from the **biradical** nature of the **p-quinodimethane** backbones
- CASSCF(6,6)/6-31G(d) calculations indicate biradical characters —**10.3%**, **7.90%**, and **13.4%** for 1, 2, and 3, respectively

Wrap-up

Key Findings

- I. SF Feasibility: All derivatives satisfy $E(S_1) \geq 2E(T_1)$ criterion.
- II. Intramolecular Charge Transfer (ICT)
 - Spectroscopy: Bathochromic shifts & quenched fluorescence and lifetimes in polar solvents indicate PICT.
 - DFT computed NTOs: Electron density shifts from phenyl (donor) to difuranone core (acceptor).
- III. Solvent polarity significantly influences the redox potentials of the chromophores, attributable to their biradical nature

These findings highlight the role of CT states in guiding the design of efficient SF materials for light-harvesting



Detailed reading: Das, B.; Sharma, R.; Kalita, A. C.; Wahab, A. *J. Phys. Chem. A* **2023**, 127, 4793–4800.



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