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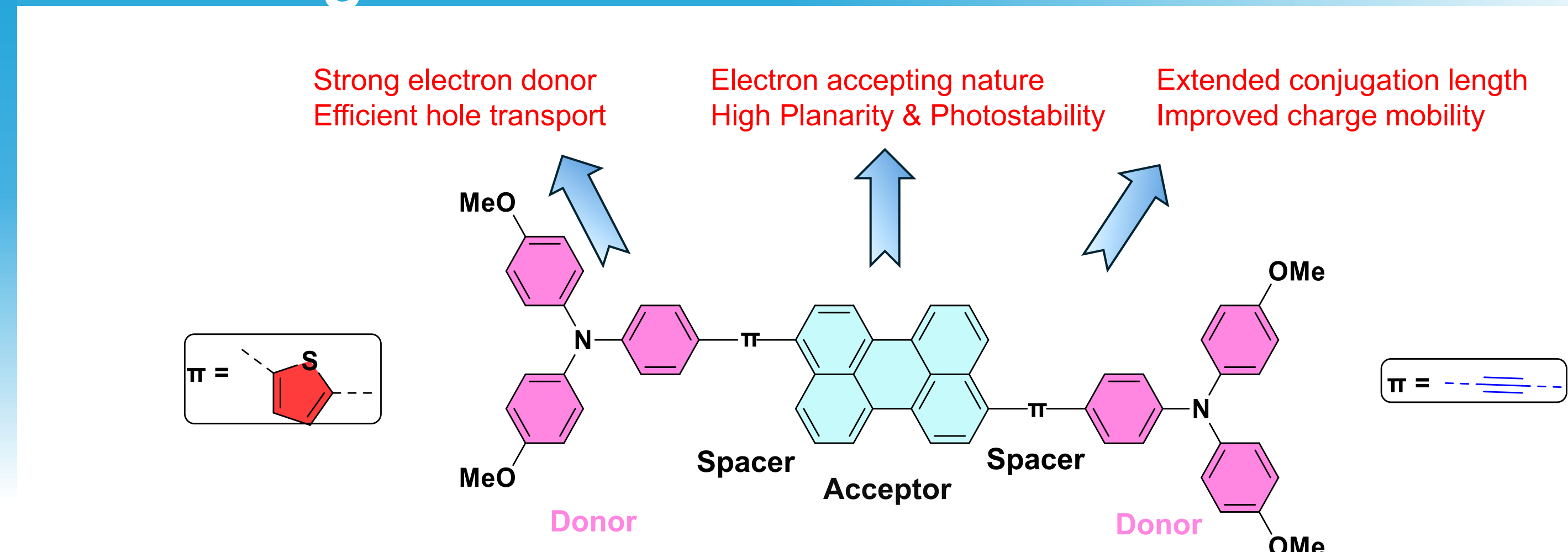
Motivation

Precise molecular design is essential for pushing the boundaries of organic optoelectronics. Perylene-based D- π -A- π -D molecules provide a versatile framework to tune photophysical and charge transport properties, critical for high-performance small-molecule semiconductors.

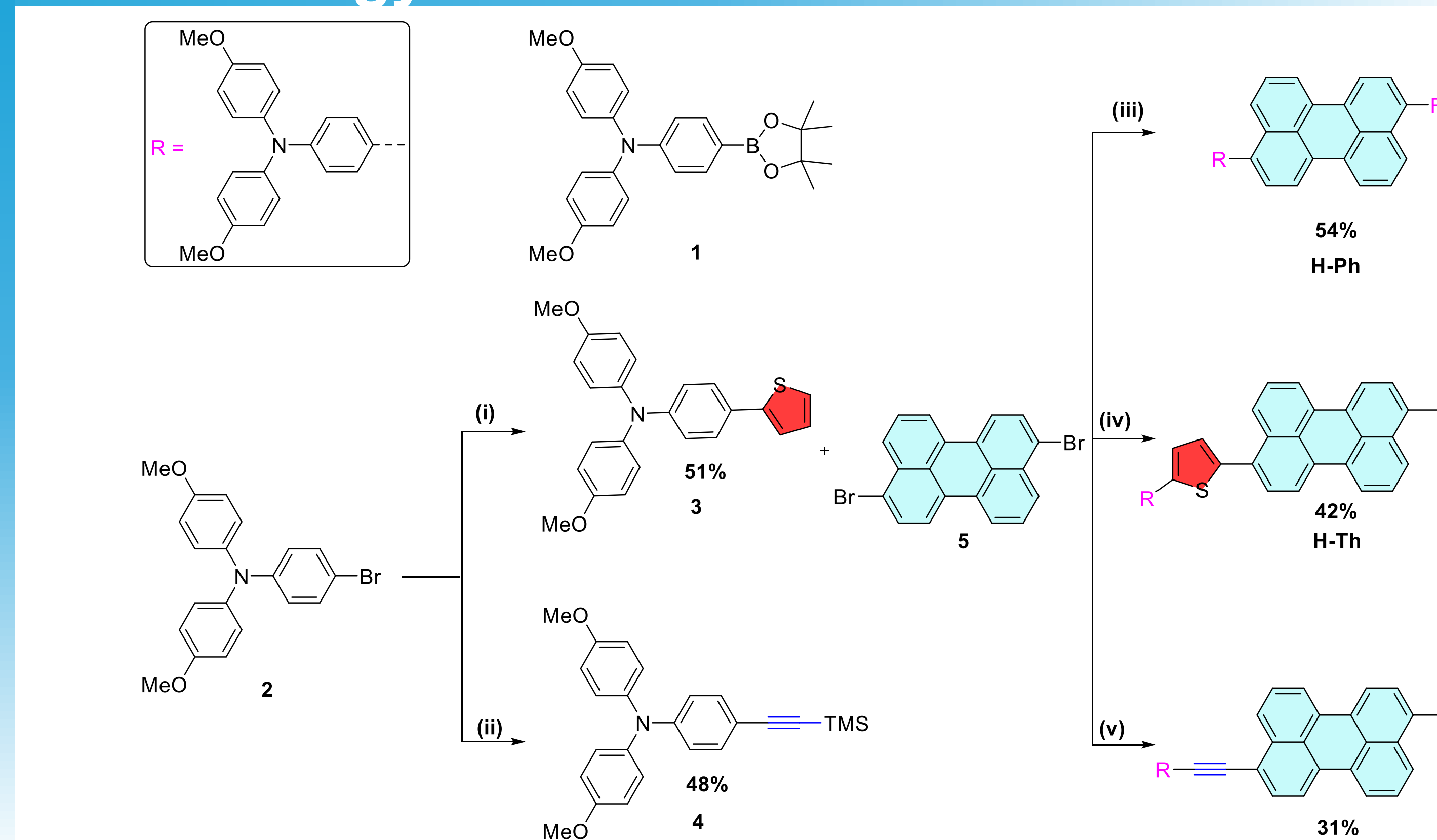
Research Question

Can π -spacer engineering (thiophene $\leftrightarrow$ ethyne) simultaneously tune intramolecular charge transfer (ICT), Stokes shift, fluorescence quantum yield, and reorganization energy to improve predicted charge transport efficiency?

Our Design : D- π -A- π -D

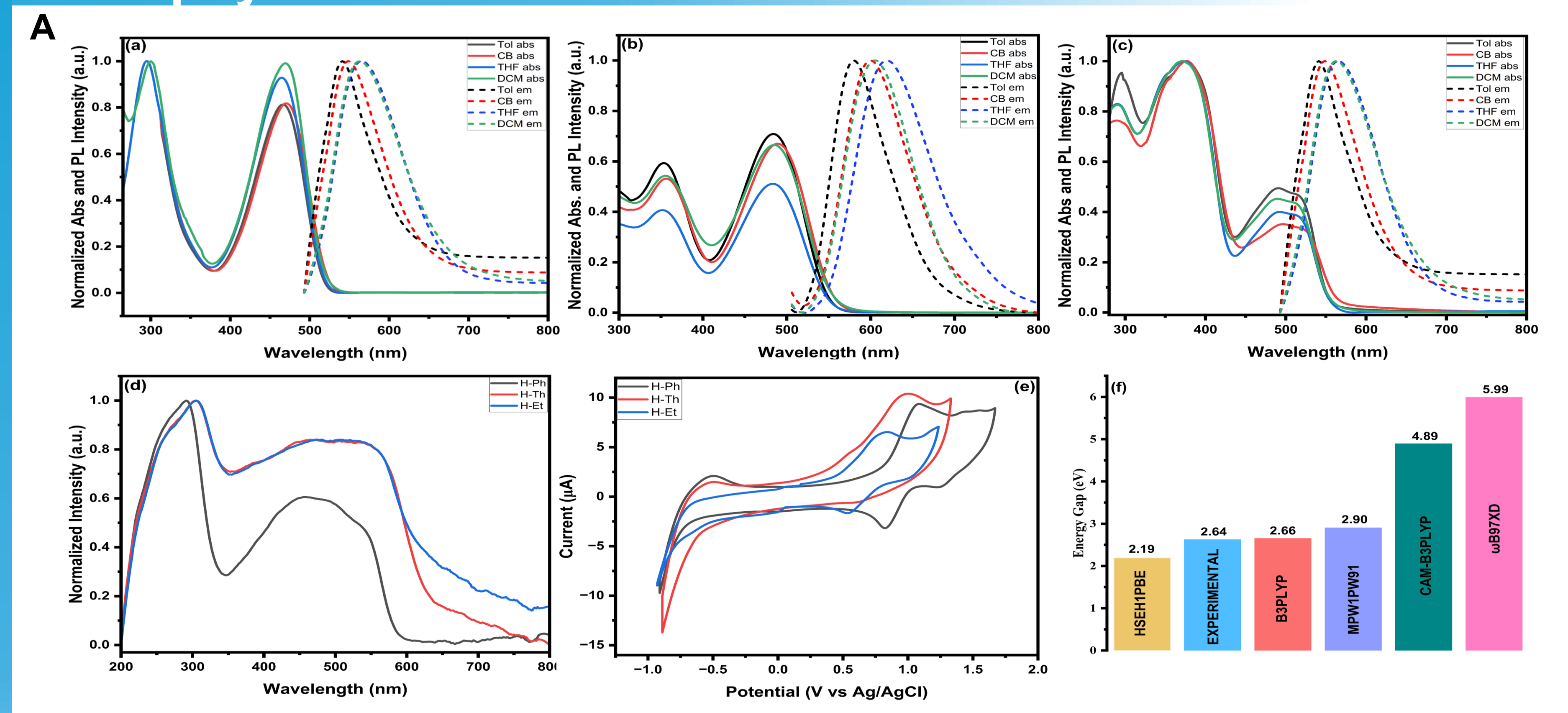


Methodology



Scheme 1. Reagents and Conditions (i) Pd(PPh₃)₂Cl₂, tributyl(thiophen-2-yl)stannane, THF, 60 °C, 6 h (ii) Pd(tBu₃P)₂, ethynyltrimethylsilane, DABCO, acetonitrile, rt, 12 h (iii) Pd(OAc)₂, SPhos, K₂CO₃, Toluene, 90 °C, 3 days (iv) Pd(OAc)₂, HPCy₃BF₄, PivOH, K₂CO₃, DMAC, 120 °C, 28 h (v) Pd(tBu₃P)₂, DABCO, Et₃N, DMF, rt, 2 days

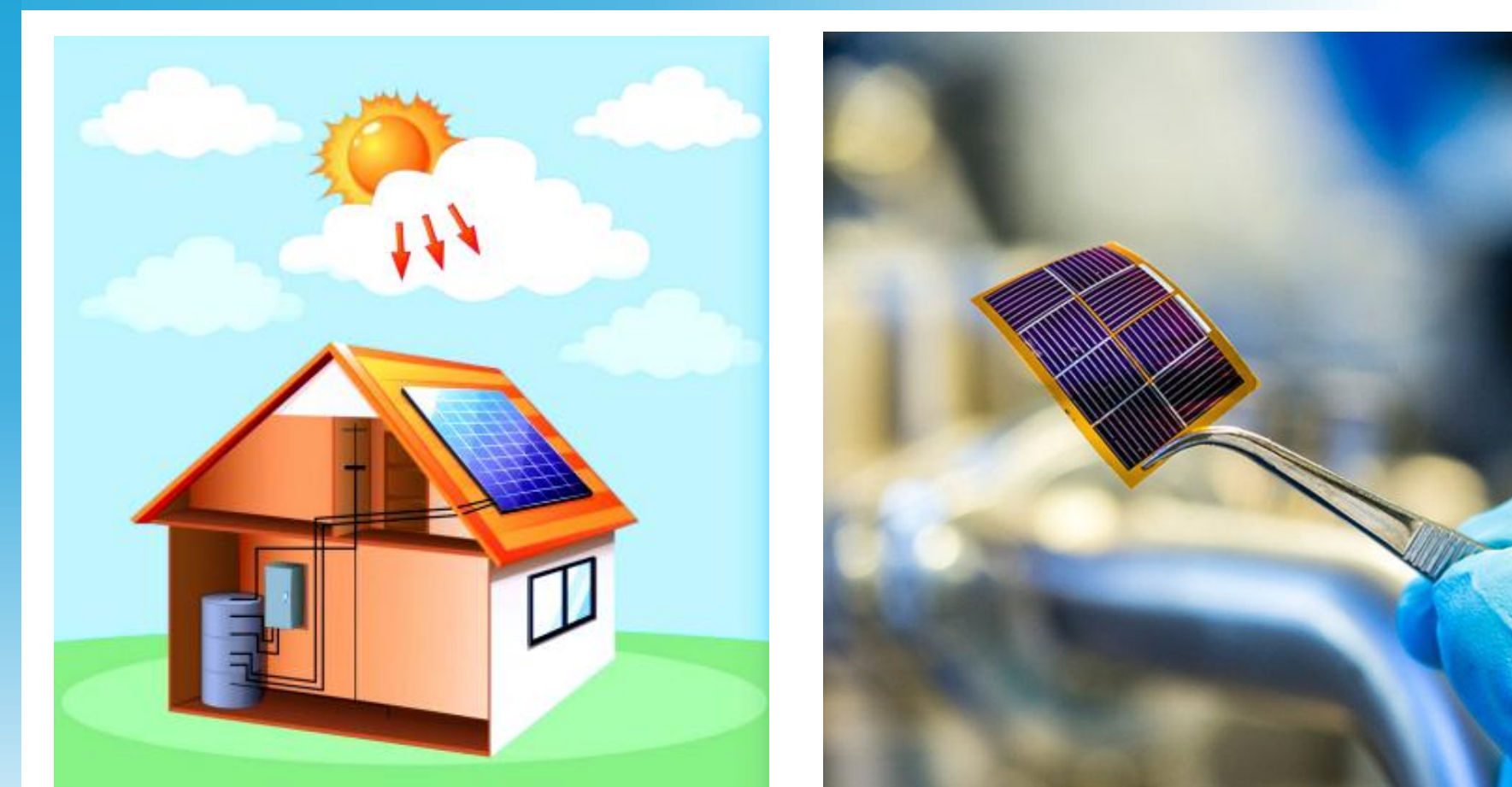
Photophysical & Electrochemical Studies



Compound	Experimental							Theoretical						
	λ_{abs} (nm)	λ_{em} (nm)	$\Delta\nu$ (cm ⁻¹)	Φ_{PL}	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	LHE	E_b (eV)	λ_h (eV)	ΔN_{max} (e)
H-Ph	468	564	3637	0.58	-5.37	-2.73	2.64	-4.76	-2.10	2.66	0.83	0.32	0.19	2.58
H-Th	480	620	4704	0.50	-5.29	-2.73	2.56	-4.74	-2.31	2.43	0.95	0.29	0.15	2.90
H-Et	490	598	3686	0.69	-5.12	-2.60	2.52	-4.68	-2.39	2.29	0.98	0.25	0.13	3.09

Figure A. (a–c) UV–Vis absorption and emission spectra in five solvents, (d) solid-state absorption, (e) cyclic voltammetry in anhydrous acetonitrile, (f) experimental vs. DFT (B3LYP/6-31+G(d,p)) band gaps for H-Ph, and an integrated summary table of experimental and theoretical parameters. (*THF solvent #Chlorobenzene solvent)

Relevant SDGs



SDG 7:
Affordable &
Clean Energy

SDG 12:
Responsible
Consumption &
Production

Acknowledgement

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- ❖ HEC – LCF-7 & NRPU 15990

References

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- ❖ H. Yaqoob, M. Nawaz, R. S. Z. Saleem and G. A. Chotana, *J. Photochem. Photobiol. A: Chem.*, 2026, 470, 116661.



Computational Studies

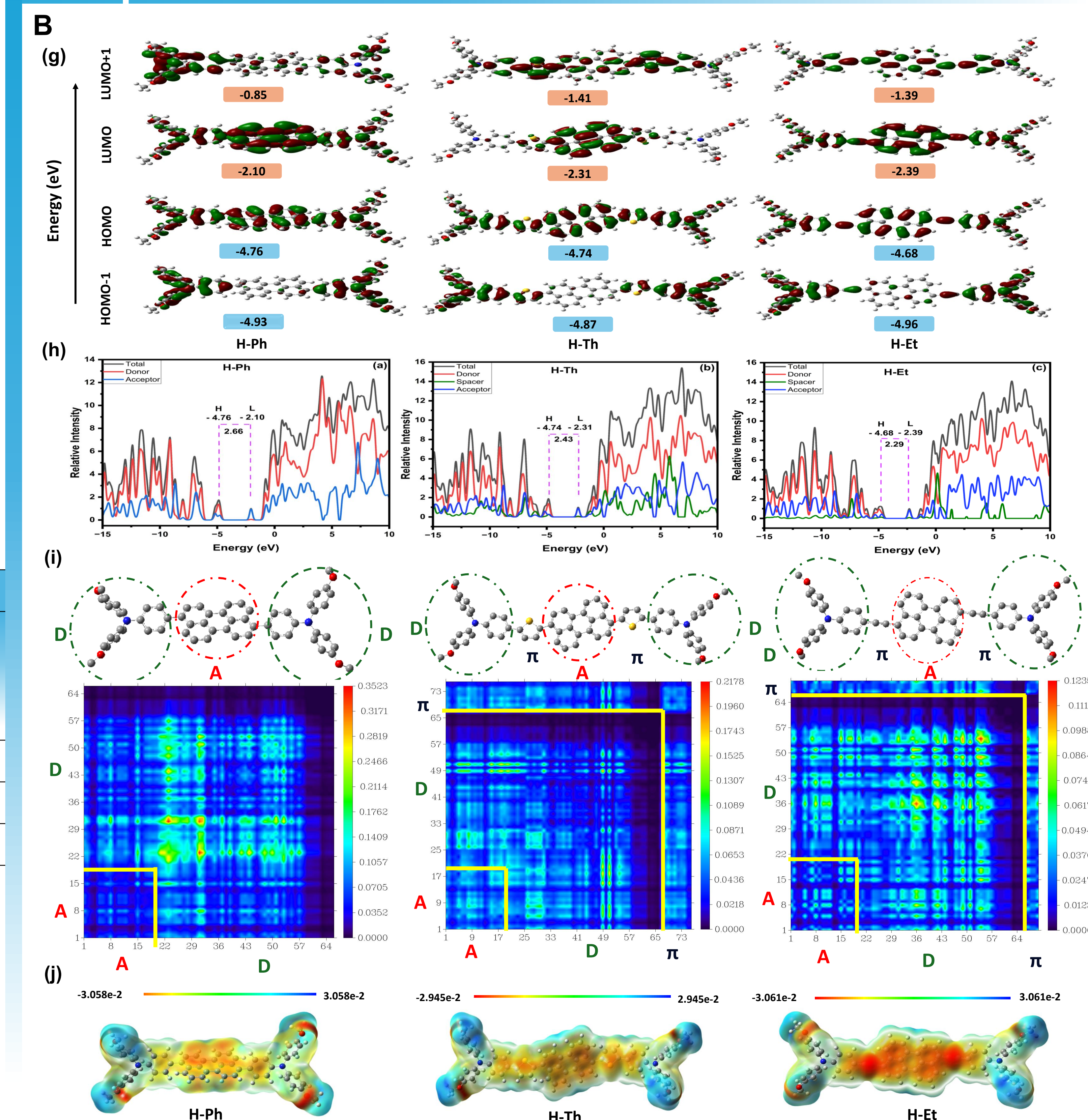


Figure B. (g) Frontier molecular orbitals (FMOs), (h) Density of states (DOS), (i) Transition density matrix (TDM) (j) Molecular electrostatic potential (MEP) analyses for synthesized compounds performed at B3LYP/6-31+G(d,p) level of theory

Conclusion

- ❖ π -spacer tuning modulates ICT character, absorption & emission properties.
- ❖ ICT absorption at 480–496 nm while emission at 562–620 nm.
- ❖ H-Th showed large Stokes shift ($\Delta\nu = 4704 \text{ cm}^{-1}$) in THF due to flexible thiophene spacer.
- ❖ H-Et exhibited higher fluorescence quantum yield ($\Phi_{PL} = 0.69$), lower reorganization & exciton-binding energies - predicted better charge mobility.