Theoretical Insights on Tunable Optoelectronics and Charge Mobilities in Cyano-Perylenediimides (PDIs): Interplays between -CN Numbers and Positions

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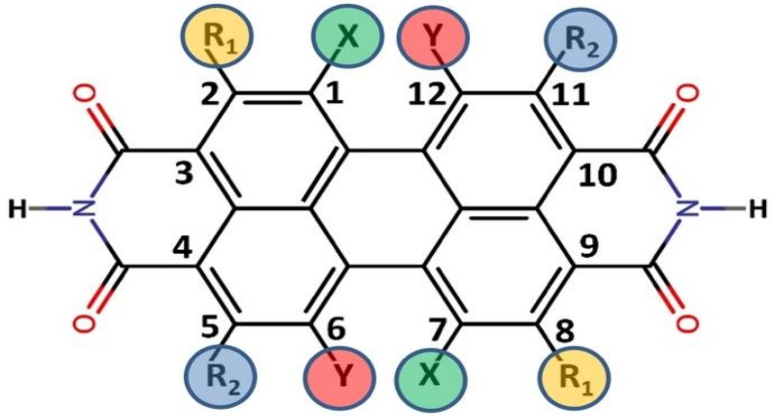


PDI-(CN)$_x$ $[x = 0, 2, 4]$

Why PDIs?

- ❖ Excellent thermal, chemical and photochemical stability
- ❖ Easy functionalization at imide-N and core positions
- ❖ Visible light absorber and highly fluorescent
- ❖ Packing diversity
- ❖ Good electron accepting ability
- ❖ Limited carrier mobility

Motivation:

Can the PDI transport be tuned *via* simple molecular means retaining its optoelectronics?

Objectives:

How and to what extent -CN substitution with varied -CN numbers and positions modulate

- ❖ Optoelectronics
- ❖ Charge Mobilities

Computational Methods

- **Ground-state : Dispersion corrected DFT (ωB97XD) with 6-311G(d,p) basis set**
- **Excited-state : TD-OTRSH (gas-phase), TD-OTSRSH+PCM (condensed-phase)**

$$E_{xc} = \alpha\, E_{Fx}^{SR} + (1-\alpha)E_{DFx}^{SR} + (\alpha+\beta)E_{Fx}^{LR} + (1-\alpha-\beta)E_{DFx}^{LR} + E_c$$ **(RSH Functional Form)**

$$\frac{1}{r} = \frac{\alpha + \beta\, erf(\omega.r)}{r} + \frac{[1-\{\alpha+\beta\, erf(\omega.r)\}]}{r}$$

Long Range (LR) **Short Range (SR)**

α = **Amount of short range fock exchange**

ω= **Range switching parameter**

ε = **Material's extended dielectric**

$\alpha = 0.2$ $\alpha+\beta = 1$ **(gas-phase)** $\alpha+\beta = \frac{1}{\varepsilon}$ **(condensed-phase)**

Optimal Tuning (OT): $J^2(\omega) = \sum_{i=N}^{N+1} [IP^{\omega}(i) + E_H^{\omega}(i)]^2$ **(Enforcing Janak's Theorem)**

Ref.: **Manna *et al., J. Chem. Theory Comput.*, 2015, 11, 1110.**

- **Charge transfer rate (k) : Semi-classical Marcus Theory**

$$k = \frac{2\pi}{\hbar}|V|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} exp\left(-\frac{\lambda}{4k_B T}\right)$$

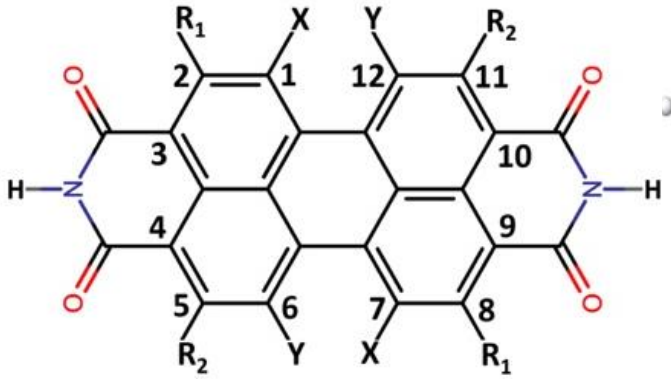
- **Carriers mobilities (μ) : Einstein-Smoluchowski equation**

$$\mu_{e/h} = \frac{qr^2}{k_B T} k_{e/h}$$

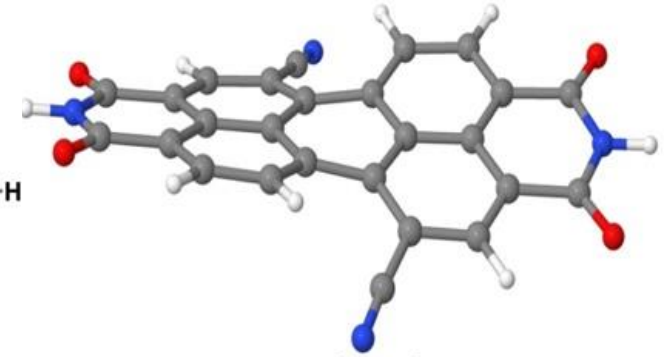
- **Reorganization energy (λ) : Nelson's four point AP method**
- **Electronic coupling (V) : CDFT-CI method**

Results and Discussion: Structures and Stability

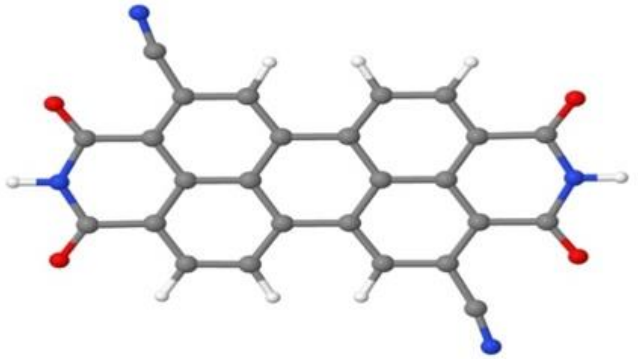
Relaxed Structures of PDI-$(CN)_x$ $[x = 0, 2, 4]$



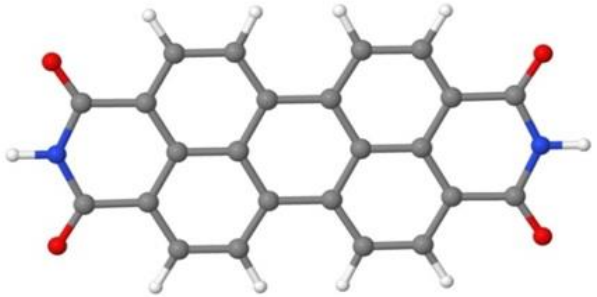
PDI-$(CN)_x$ $[x = 0, 2, 4]$



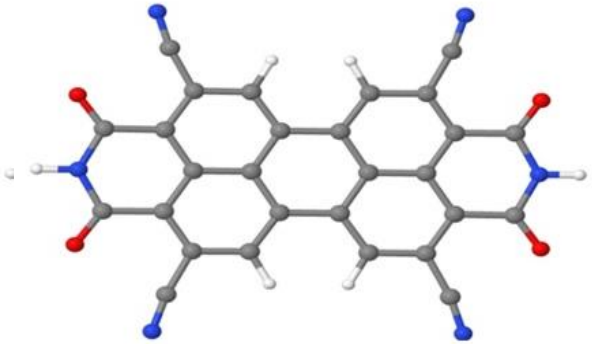
PDI-$(CN)_2$-a
ϕ = 19.1°
$\mu = 1.98$ D



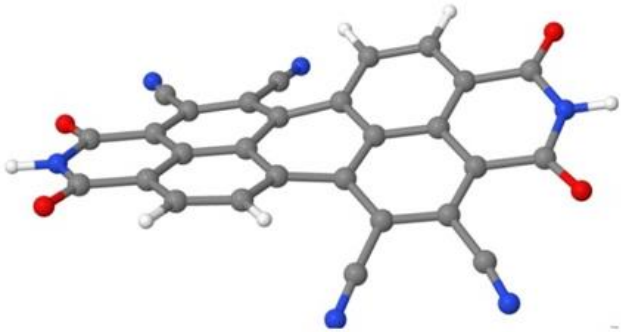
PDI-$(CN)_2$-b
ϕ = 0°
$\mu = 0.00$ D



Pristine-PDI
ϕ = 0°
$\mu = 0.00$ D



PDI-$(CN)_4$-a
ϕ = 0°
$\mu = 0.00$ D



PDI-$(CN)_4$-b
ϕ = 22.5°
$\mu = 4.05$ D

Smaller Molecular Dipole

↓

Reduced Charge Trapping

Finite Local Dipoles

↓

Better Stacking

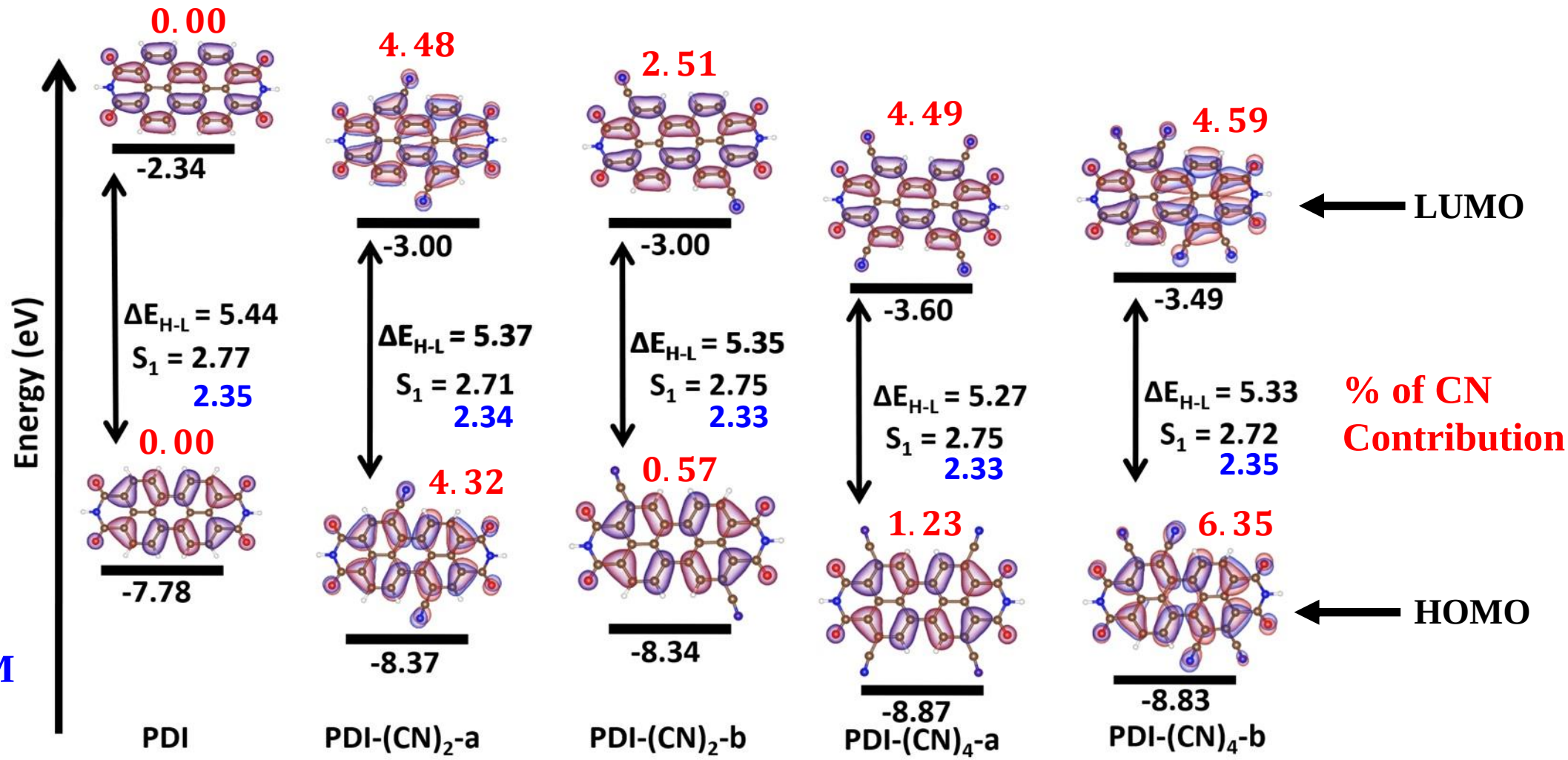
Expt. Ref.: Gao *et al.*, *Org. Lett.*, 2014, 16, 394.

Results and Discussion: Optoelectronic Properties

Gas-phase S_1: OTRSH

$S_1^{Expt.}$(PDI) = 2.34*

Condensed-phase S_1: OTSRSH+PCM



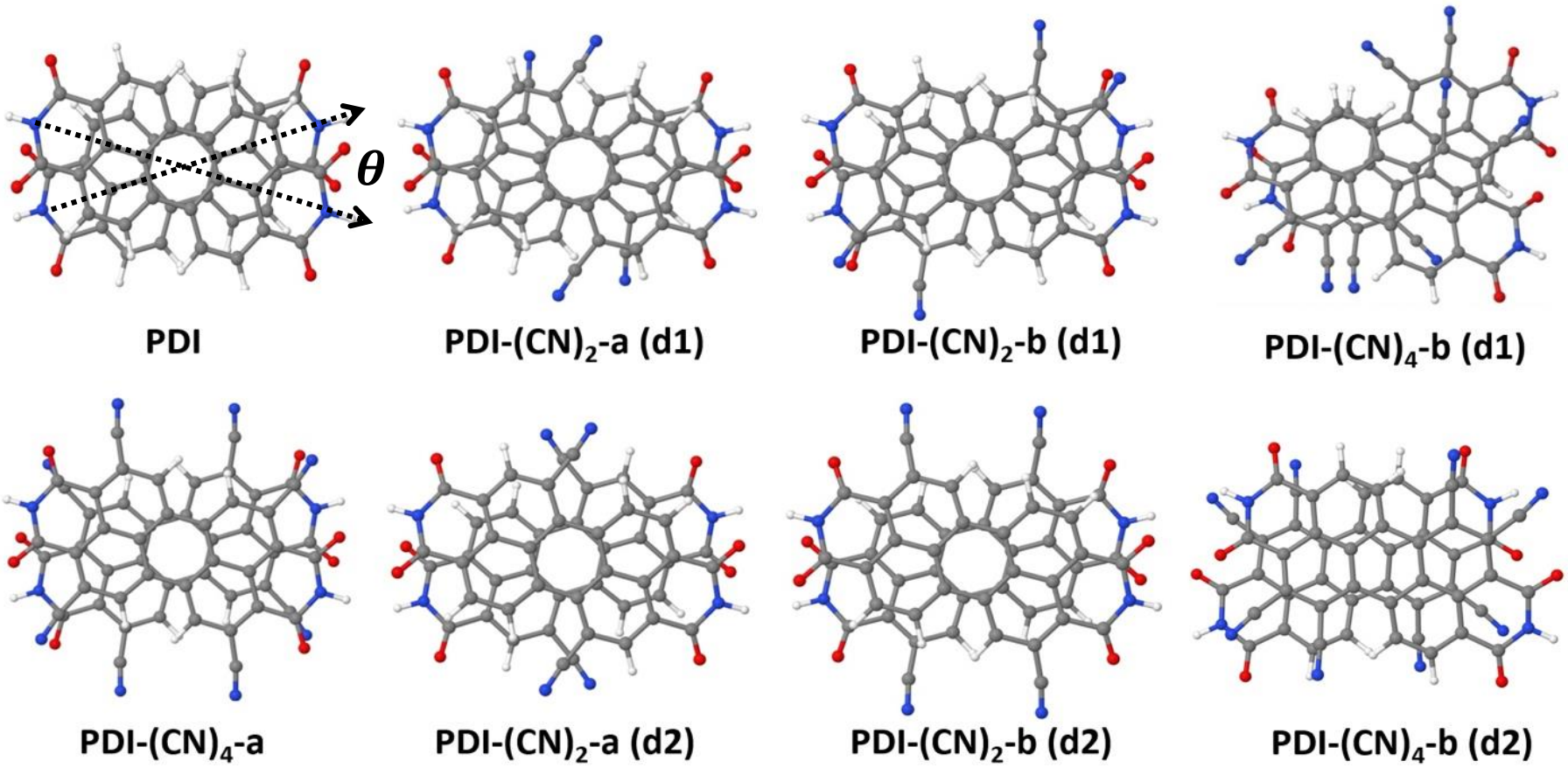
✓ Better Electron Accepting Ability ✓ Enhanced Oxidative Stability ✓ Similar Fundamental and Optical Gaps

*Expt. Ref.: Kim *et al.*, *J. Phys. Chem. Lett.*, 2020, 11, 3934.

Results and Discussion: Dimer Structural Stability

Relaxed Dimer Structures (Top view)

- Stacking distance ~ 3.4 Å
- Angle (θ) ~ 29.5°-34.1°
- E_b ~ −27.5-31.3 kcal mol^{-1}
- vdW ~ − 33.9-40.1 kcal mol^{-1}



✓ All the dimers form stable structure

✓ Stability is governed by vdW interaction

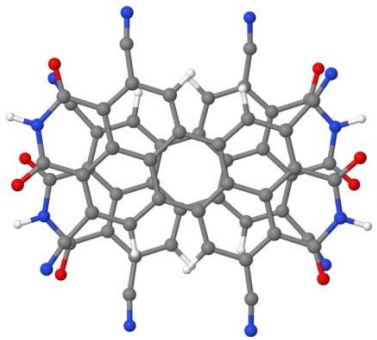
Expt. Ref. of X-Ray Crystal data for PDI: Burgdorff *et al.*, *Chem. Phys. Lett.*, 1992, 197, 358.

Results and Discussion: Charge Mobilities

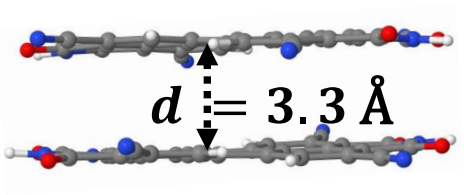
Carriers Mobilities of PDIs

Systems	Carriers Mobility $cm^2/(V\text{-}s)$	
	μ_e	μ_h
Pristine-PDI	0.10*	2.70
PDI-$(CN)_2$-a (d1)	3.84×10^{-6}	1.01
PDI-$(CN)_2$-a (d2)	0.47	6.14
PDI-$(CN)_2$-b (d1)	0.33	5.67
PDI-$(CN)_2$-b (d2)	1.66×10^{-2}	2.58
PDI-$(CN)_4$-a	0.44	5.61
PDI-$(CN)_4$-b (d1)	2.68×10^{-2}	1.19×10^{-2}
PDI-$(CN)_4$-b (d2)	1.18	0.35

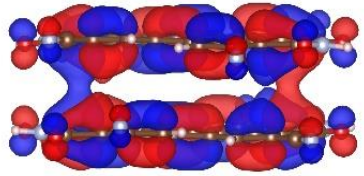
PDI-$(CN)_4$-a



Top view



Side view

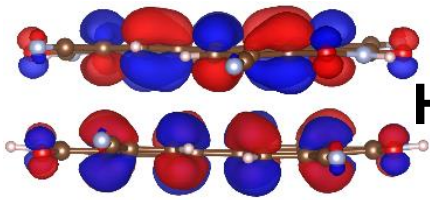


LUMO

5.39 -CN%

96 V_e

336 λ_e } meV



HOMO

2.00 -CN%

170 V_h

215 λ_h } meV

Large $V_{e/h}$ + Smaller $\lambda_{e/h}$

↓

Greater $\mu_{e/h}$

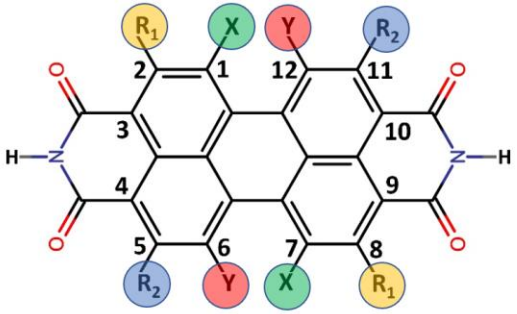
PDI charge mobilities are considerably modulated by –CN

$\mu_e^{Expt.}$(PDI) = 0.10 $cm^2/(V\text{-}s)$*

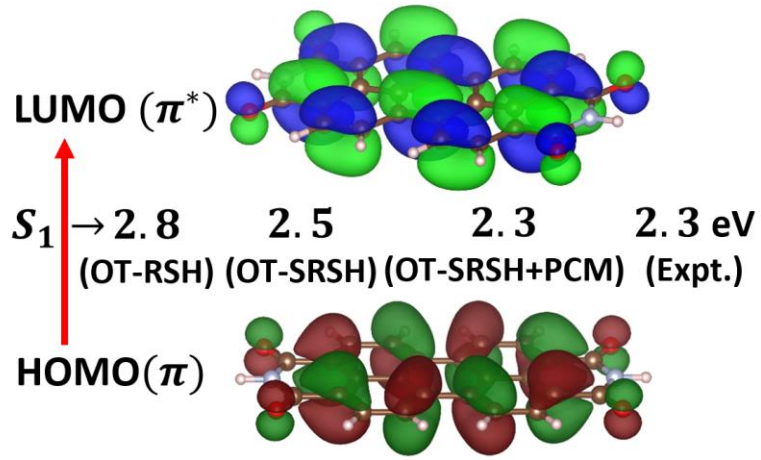
*Expt. Ref.: Zhan *et al., Adv. Mater.*, 2010, 23, 268.

Conclusion

- CN-substituted PDIs show better electron accepting ability and enhanced oxidative stability.
- Optoelectronic properties are only marginally affected by the CN-functionalization.
- OTSRSH+PCM correctly reproduces the condensed-phase optical peak position.
- In general, smaller λ_e and λ_h are found upon CN-functionalization.
- Better stacked dimers exhibit greater V_e and V_h.
- PDI-$(CN)_4$-a exhibits very large μ_h and μ_e.



PDI-$(CN)_x$ $[x = 0, 2, 4]$



- ➢ Better Non-Fullerene Acceptors
- ➢ Enhanced Oxidative Stability
- ➢ Retaining Optoelectronics
- ➢ Improved Charge Transport

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Thank You