

Supporting Information

Impact of chemical modifications on the luminescence properties of organic neutral radical emitters

Eunkyung Cho, Veaceslav Coropceanu,* and Jean-Luc Brédas*

Department of Chemistry and Biochemistry
The University of Arizona
Tucson, Arizona 85721-0088

Dedicated to Professor Concepció Rovira and Professor Jaume Veciana, in honor of their seminal contributions to the fields of molecular electronics and magnetism.

* Email: coropceanu@arizona.edu; jlbredas@arizona.edu

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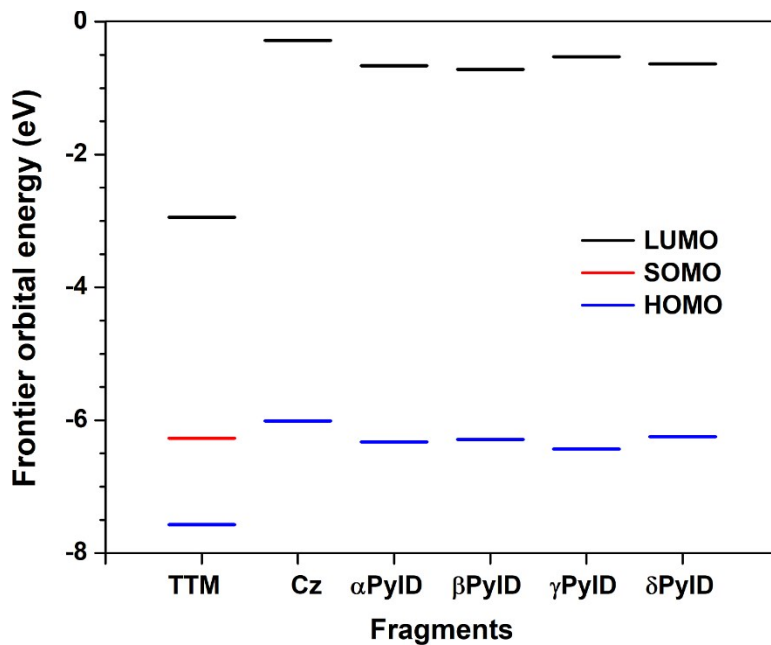


Figure S1. Energies of the LUMO, SOMO, and doubly occupied HOMO levels in the TTM and donor (isolated) fragments.

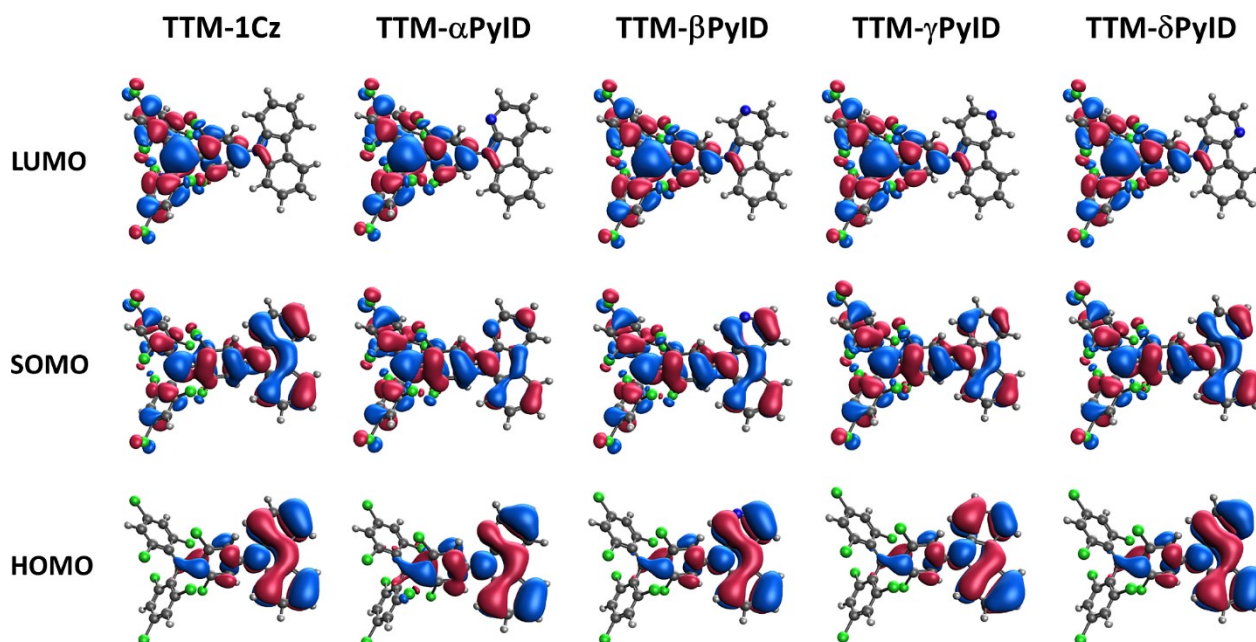


Figure S2. Frontier molecular orbitals of the TTM-1Cz and TTM-xPyID radicals.

Table S1. Vertical excitation energies (E), transition dipole moments (μ), and oscillator strengths (f) of the lowest ten doublet and lowest quartet excited states in the TTM radical.

	E (eV)	μ (D)	f
D₁	2.82	1.62	0.03
D₂	2.82	1.62	0.03
D ₃	3.10	0.89	0.01
D ₄	3.10	0.62	0.00
D ₅	3.10	0.62	0.00
D ₆	3.29	0.00	0.00
D₇	3.55	4.07	0.22
D₈	3.55	4.07	0.22
D ₉	3.74	1.05	0.02
D ₁₀	3.92	0.50	0.00
Q ₁	3.96	0.00	0.00

Table S2. Vertical excitation energies (in eV) and (in parentheses) transition dipole moments (in D) of the CT, LE₁, LE_{r1}, and LE_{r2} states of the TTM-1Cz and TTM-xPyID radicals.

State	TTM-1Cz	TTM- α PyID	TTM- β PyID	TTM- γ PyID	TTM- δ PyID
D ₁ (CT)	2.19 (3.71)	2.45 (3.55)	2.33 (3.53)	2.40 (3.31)	2.30 (3.59)
D _{2 or 3} [#] (LE ₁)	2.82 (1.45)	2.82 (1.28)	2.81 (1.55)	2.80 (1.57)	2.81 (1.49)
D ₈ (LE _{r1})	3.31 (3.68)	3.37 (4.18)	3.33 (3.11)	3.33 (3.58)	3.32 (3.43)
D _{9 or 10} [*] (LE _{r2})	3.49 (3.96)	3.49 (3.95)	3.51 (3.91)	3.52 (3.75)	3.50 (3.95)

[#] The D₂ states of the TTM-xPyID radicals and D₃ state of TTM-1Cz are assigned as LE₁. ^{*} The D₁₀ states of all radicals except TTM- α PyID are assigned as LE_{r2}; LE_{r2} in the TTM- α PyID is the D₉ state.

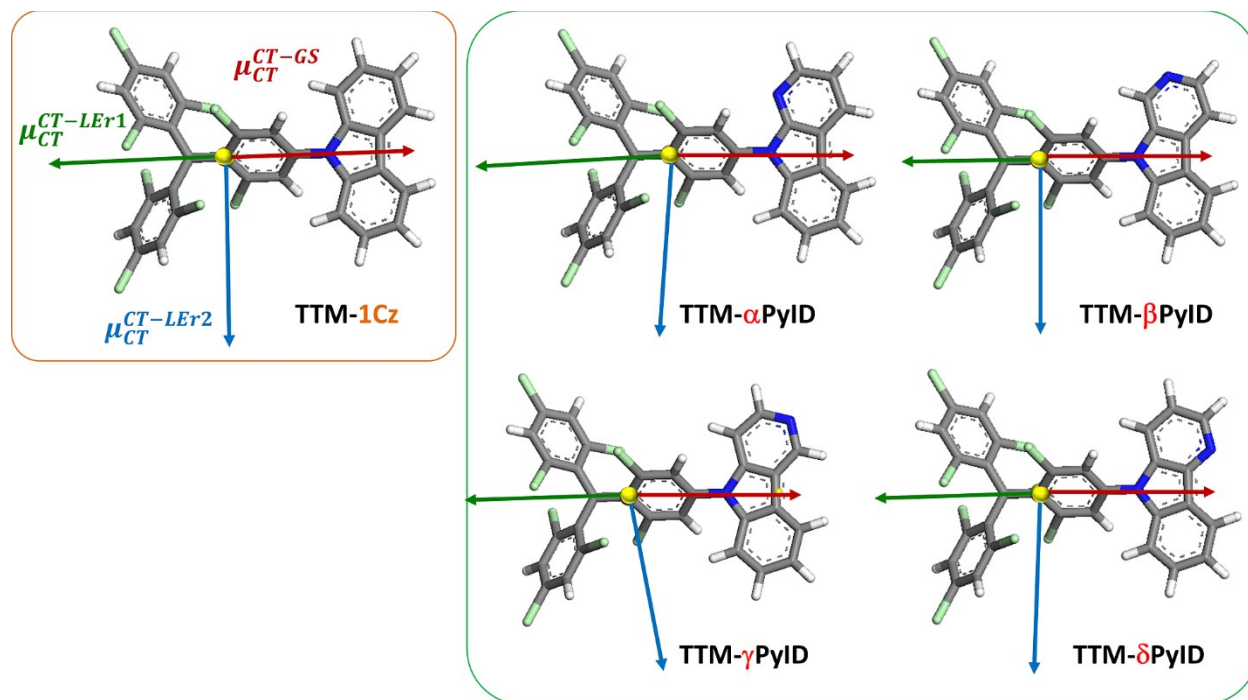


Figure S3. Schematic description of the contributions to the transition dipole moments in the CT state due to CT-GS hybridization (μ_{CT}^{CT-GS} , red arrows), CT-LE_{r1} hybridization ($\mu_{CT}^{CT-LEr1}$, green arrows), and CT-LE_{r2} hybridization ($\mu_{CT}^{CT-LEr2}$, blue arrows) for the TTM-1Cz and TTM-xPyID radicals; yellow dots indicate the center-of-mass for each molecule.

Table S3. Adiabatic CT energies (E_{CT}^a), electronic coupling values (V_{CT-GS}), and reorganization energies (λ) between the CT and ground states in the TTM-1Cz and TTM-xPyID radicals.

state	TTM-1Cz	TTM- α PyID	TTM- β PyID	TTM- γ PyID	TTM- δ PyID
V_{CT-GS} (meV)	314	435	336	342	337
E_{CT}^a (eV)	1.94	2.31	2.12	2.17	2.09
λ (eV)	0.27	0.15 [#]	0.24	0.29	0.25

[#] The geometry optimization calculation of the CT state in TTM- α PyID yielded unreliable results. Thus, based on the data shown in Table S5, we set the λ value in TTM- α PyID equal to the average value of TTM- β PyID and TTM- δ PyID, *i.e.*, 0.25 eV.

Table S4. Nonradiative decay rates (k_{nr}^{CT-GS}) from the coupling between the CT and ground states in the TTM-1Cz and TTM-xPyID radicals calculated by considering different amounts of quantum contributions (λ_{qm}) to the total reorganization energy λ ; λ_{qm} is assigned to 0, 10, 20, and 50% of λ .

λ_{qm}	k_{nr}^{CT-GS} (s ⁻¹)			
	0% of λ	10% of λ	20% of λ	50% of λ
TTM-1Cz	1.59×10^{-28}	4.30×10^1	2.19×10^3	4.35×10^6
TTM- α PyID	4.41×10^{-56}	1.58×10^{-3}	2.94×10^{-1}	3.53×10^3
TTM- β PyID	7.10×10^{-47}	2.47×10^{-3}	1.18×10^1	2.74×10^4
TTM- γ PyID	2.97×10^{-36}	2.86×10^{-1}	1.26×10^2	2.76×10^5
TTM- δ PyID	6.45×10^{-42}	3.84×10^{-1}	3.59×10^1	1.22×10^5

Table S5. Relaxation energies of the TTM and donor fragments in the neutral state and charged state, λ_{rel-N} (meV) and λ_{rel-C} (meV), obtained from the adiabatic potential surfaces of both neutral and charged states and from a normal-mode analysis; the charged states of the TTM and donor (Cz and xPyID) fragments correspond to the anion and cation states, respectively.

	Adiabatic potential surface		Normal mode	
	λ_{rel-N}	λ_{rel-C}	λ_{rel-N}	λ_{rel-C}
TTM	109	121	108	125
Cz	61	61	62	60
α PyID	67	62	68	62
β PyID	65	64	66	64
γ PyID	135	126	136	129
δ PyID	70	66	71	67