

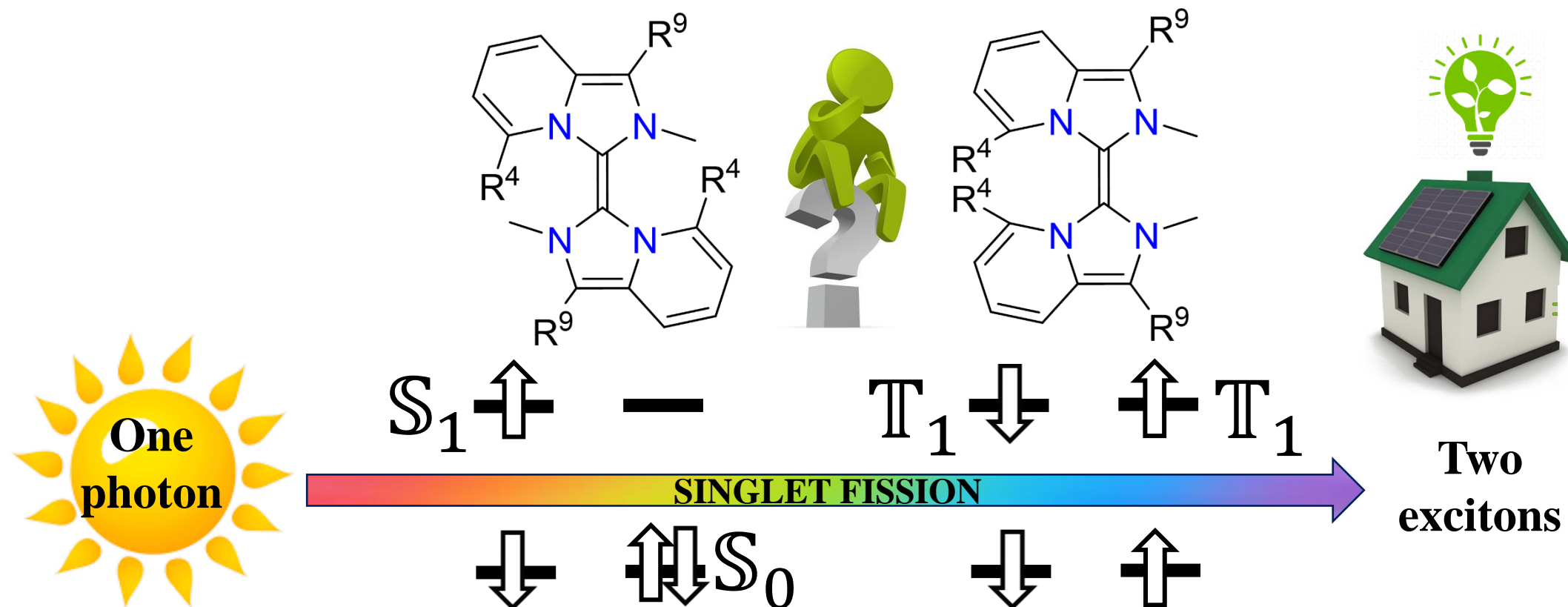
CARBENE DIMERS - THINKER TOYS FOR DESIGNING SINGLET FISSION MATERIALS FOR EFFICIENT ORGANIC SOLAR CELLS



Gergana Kostadinova, Rumen Lyapchev, Alia Tadjer, Ilia Kichev and Julia Romanova

^a University of Sofia, Faculty of Chemistry and Pharmacy, Sofia 1164, Bulgaria

*jromanova@chem.uni-sofia.bg



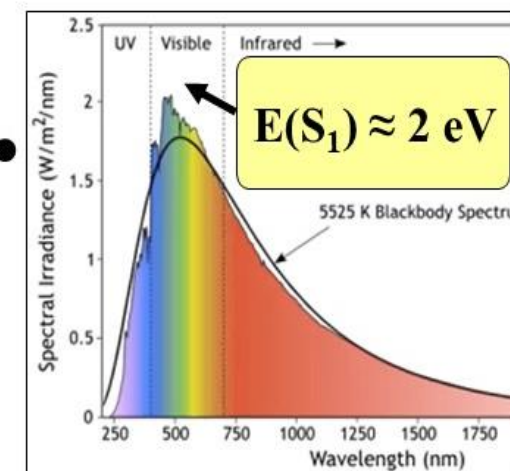
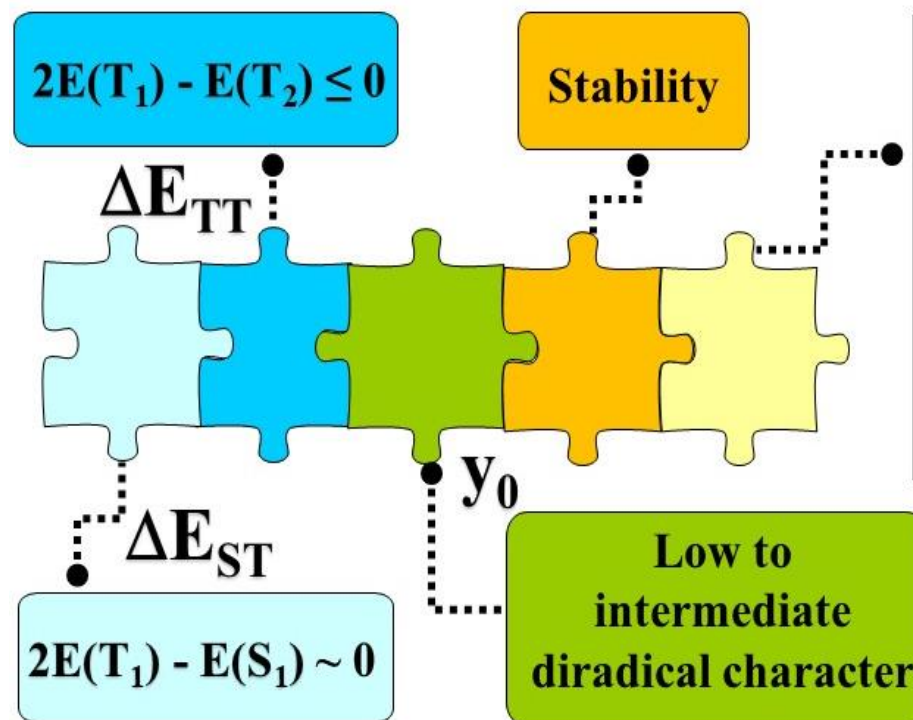
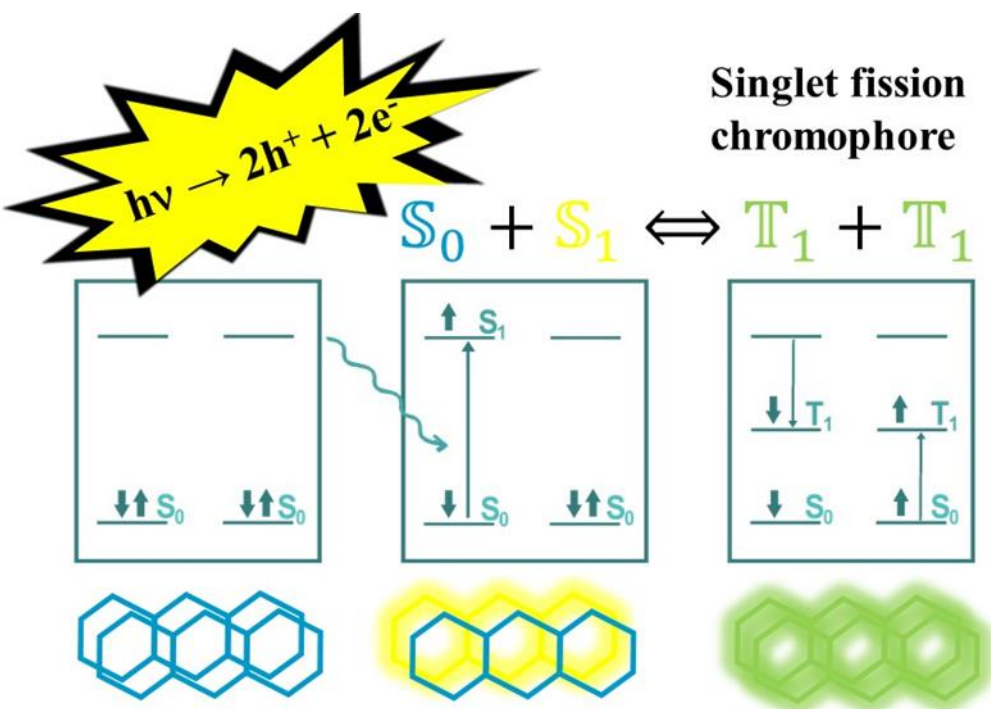
CARBENE DIMERS - THINKER TOYS FOR DESIGNING SINGLET FISSION MATERIALS FOR EFFICIENT ORGANIC SOLAR CELLS



Gergana Kostadinova, Rumén Lyapchev, Alia Tadjer, Ilia Kichev and Julia Romanova

^a University of Sofia, Faculty of Chemistry and Pharmacy, Sofia 1164, Bulgaria

*jromanova@chem.uni-sofia.bg



CARBENE DIMERS - THINKER TOYS FOR DESIGNING SINGLET FISSION MATERIALS FOR EFFICIENT ORGANIC SOLAR CELLS



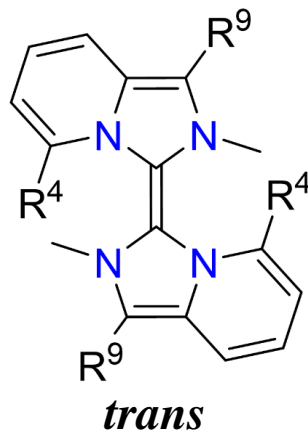
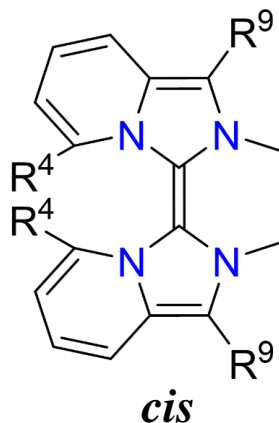
Gergana Kostadinova, Rumen Lyapchev, Alia Tadjer, Ilia Kichev and Julia Romanova

^a University of Sofia, Faculty of Chemistry and Pharmacy, Sofia 1164, Bulgaria

*jromanova@chem.uni-sofia.bg

Table 1. Feasibility conditions for singlet fission - ΔE_{ST} [eV] and ΔE_{TT} [eV] in N-heterocyclic carbene dimers.

Substituent	Form	ΔE_{ST}	ΔE_{TT}
4,9-H	<i>trans</i>	0.37	0.66
4,9-H	<i>cis</i>	-0.19	-0.07
4-C≡CH, 9-H	<i>trans</i>	0.14	0.53
4-C≡CH, 9-H	<i>cis</i>	-1.10	-0.84
4-C≡N, 9-H	<i>trans</i>	0.03	0.42
4-C≡N, 9-H	<i>cis</i>	-1.36	-1.10
4-C≡CPh, 9-H	<i>trans</i>	0.11	0.45
4-C≡CPh, 9-H	<i>cis</i>	-1.05	-0.97
4-C≡C-C≡CH, 9-H	<i>trans</i>	-0.02	0.33
4-C≡C-C≡CH, 9-H	<i>cis</i>	-1.12	-0.92
4-H, 9-C≡CH	<i>trans</i>	0.37	0.66
4-H, 9-C≡CH	<i>cis</i>	-0.27	-0.16
4-H, 9-C≡N	<i>trans</i>	0.48	0.74
4-H, 9-C≡N	<i>cis</i>	-0.23	-0.13
4-H, 9-C≡CPh	<i>trans</i>	0.36	0.61
4-H, 9-C≡CPh	<i>cis</i>	-0.29	-0.20
4-H, 9-C≡C-C≡CH	<i>trans</i>	0.36	0.64
4-H, 9-C≡C-C≡CH	<i>cis</i>	-0.34	-0.23



- ✓ DFT/TDDFT
- ✓ B3LYP
- ✓ CC-PVDZ

Table 2. Free energy differences between *cis* and *trans* conformations of N-heterocyclic carbene dimers, $\Delta G_{trans-cis} = G_{trans} - G_{cis}$ [kcal/mol].

Substituent	$\Delta G_{trans-cis}$
4,9-H	-0.60
4-H, 9-C≡CH	0.29
4-H, 9-C≡N	1.15
4-H, 9-C≡C-Ph	0.00
4-H, 9-C≡C-C≡CH	0.32
4-C≡CH, 9-H	-3.23
4-C≡N, 9-H	-1.43
4-C≡CPh, 9-H	-1.10
4-C≡C-C≡C-H, 9-H	-1.78

CARBENE DIMERS - THINKER TOYS FOR DESIGNING SINGLET FISSION MATERIALS FOR EFFICIENT ORGANIC SOLAR CELLS



Gergana Kostadinova, Rumén Lyapchev, Alia Tadjer, Ilia Kichev and Julia Romanova

^a University of Sofia, Faculty of Chemistry and Pharmacy, Sofia 1164, Bulgaria

*jromanova@chem.uni-sofia.bg

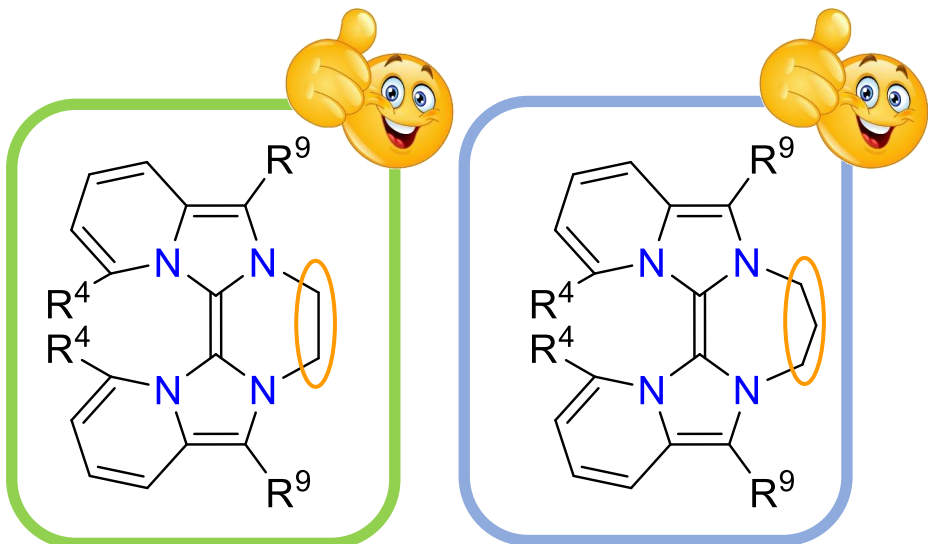


- ✓ DFT/TDDFT
- ✓ B3LYP
- ✓ CC-PVDZ

Table 3. Feasibility conditions for singlet fission - ΔE_{ST} [eV] and ΔE_{TT} [eV] in locked N-heterocyclic carbene dimers.

Bridge; Substituent	ΔE_{ST}	ΔE_{TT}
CH₂-CH₂; 4-C≡N, 9-H	-0.35	-0.04
CH₂-CH₂; 4-C≡C-C≡CH, 9-H	-0.38	-0.14
CH₂-CH₂-CH₂; 4-C≡CH, 9-H	-0.17	0.01
CH₂-CH₂-CH₂; 4-C≡N, 9-H	-0.39	-0.23
CH₂-CH₂-CH₂; 4-C≡C-C≡CH, 9-H	-0.46	-0.31

- The -C≡CH, -C≡N and -C≡C-C≡CH derivatives absorb at 1218-1360 nm, 1428-1548 nm and 1756-2168 nm, respectively.
- The compounds with -C≡CH and -C≡N functional groups absorb also in the range 419-426 nm, while the molecules containing -C≡C-C≡CH substituents possess bands at 536-548 nm.



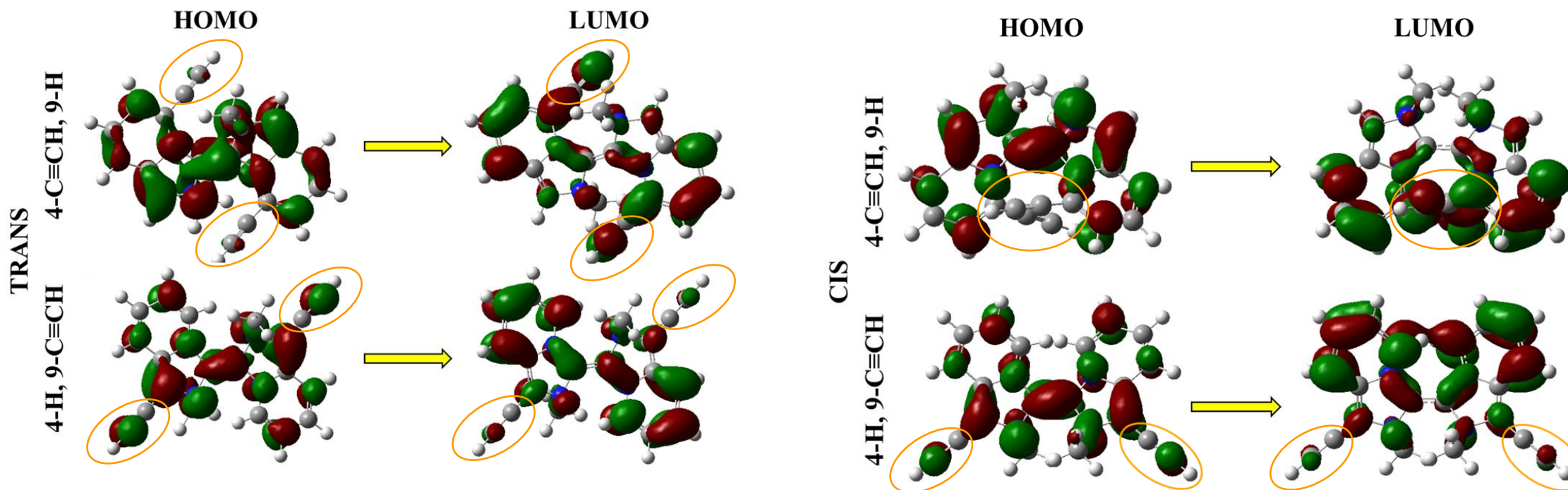
CARBENE DIMERS - THINKER TOYS FOR DESIGNING SINGLET FISSION MATERIALS FOR EFFICIENT ORGANIC SOLAR CELLS



Gergana Kostadinova, Rumén Lyapchev, Alia Tadjer, Ilia Kichev and Julia Romanova

^a University of Sofia, Faculty of Chemistry and Pharmacy, Sofia 1164, Bulgaria

*jromanova@chem.uni-sofia.bg



For compounds functionalized at position 4, charge transfer to the substituent in excited state is observed (the coefficients on the -C≡CH functional groups are almost zero in HOMO and large in LUMO).

CARBENE DIMERS - THINKER TOYS FOR DESIGNING SINGLET FISSION MATERIALS FOR EFFICIENT ORGANIC SOLAR CELLS



Gergana Kostadinova, Rumén Lyapchev, Alia Tadjer, Ilia Kichev and Julia Romanova

^a University of Sofia, Faculty of Chemistry and Pharmacy, Sofia 1164, Bulgaria

*jromanova@chem.uni-sofia.bg

https://ml4sf.chem.uni-sofia.bg/?page_id=53&lang=en

ACKNOWLEDGEMENTS



KП-06-H39/2, 09.12.2019



J.R. is grateful for the L'Oréal - UNESCO national fellowship "Women in Science" 2019 (Bulgaria).