Supporting Information for Describing Chemical Reactivity with Frontier Molecular Orbitalets

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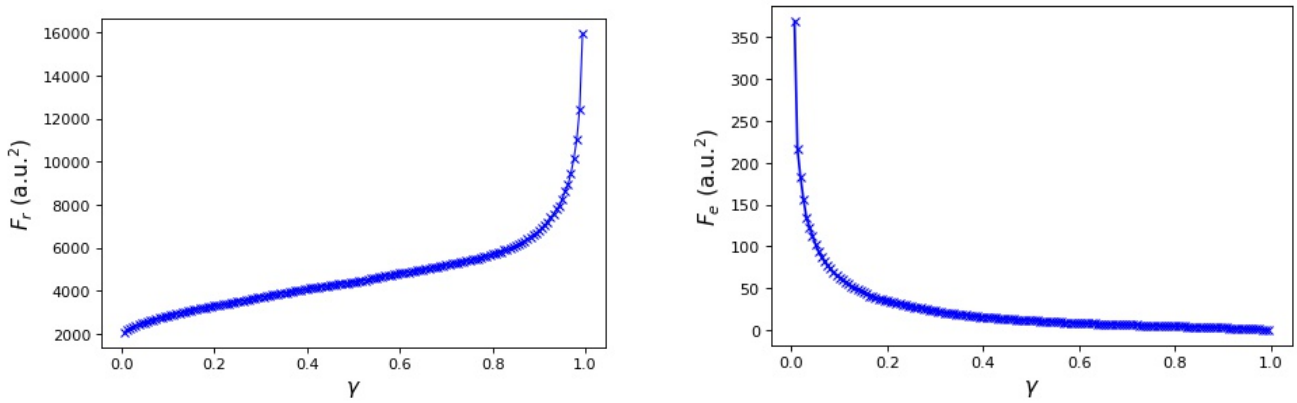
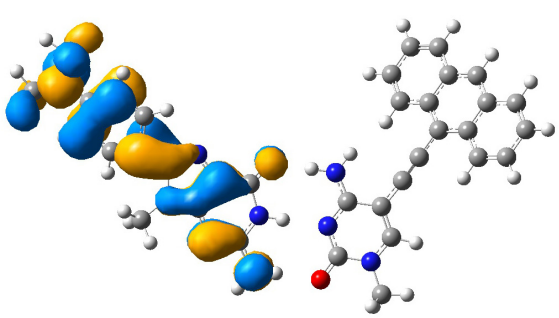


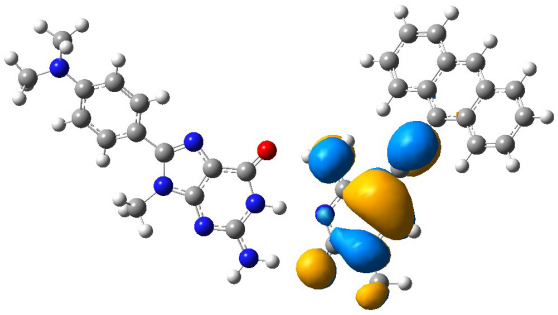
(a) Delocalization in physical space

(b) Delocalization in energy space

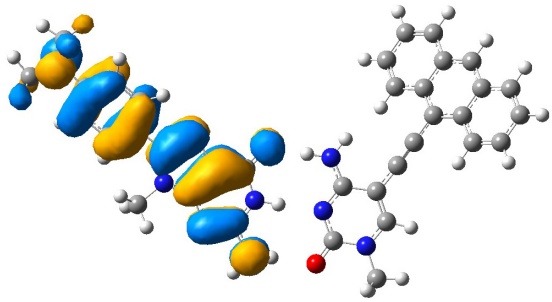
Figure S1: F_r and F_e of hexadecaoctaene. (a) F_r is plotted as a function of γ, the value increases as γ increases. (b) F_e is plotted as a function of γ, the value decreases as γ increases.



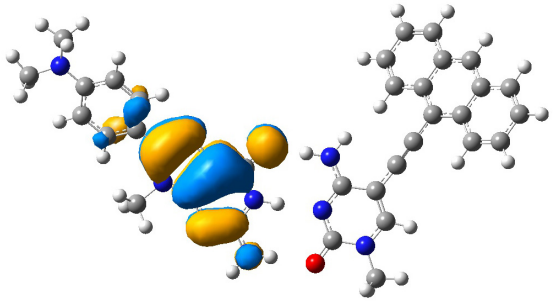
(a) HOMO−2



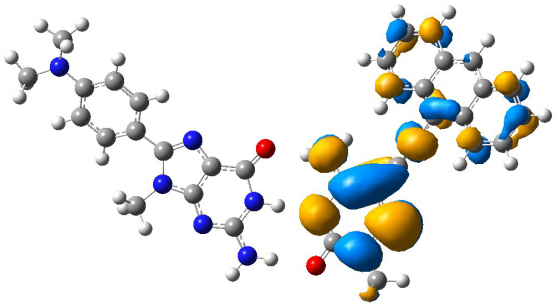
(b) HOMOL−2



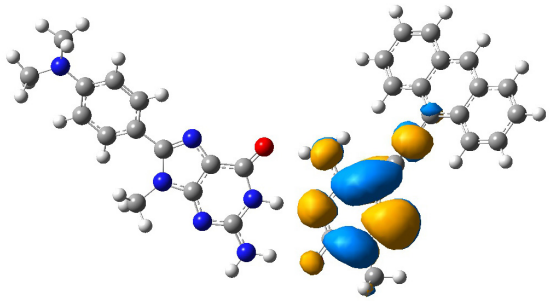
(c) HOMO



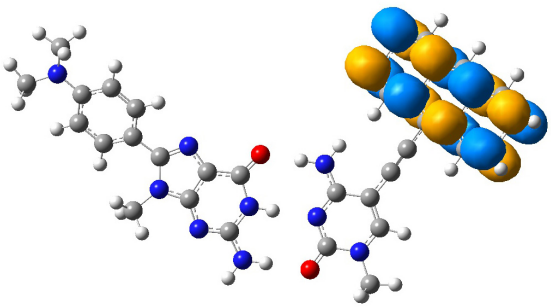
(d) HOMOL



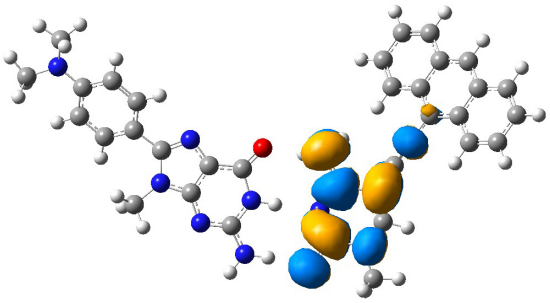
(e) LUMO+1



(f) LUMOL+1

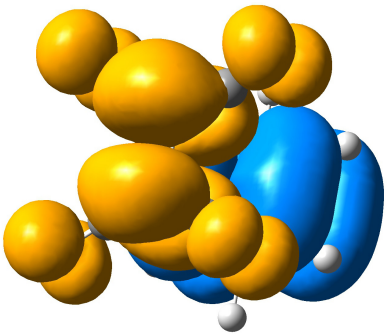


(g) LUMO+2

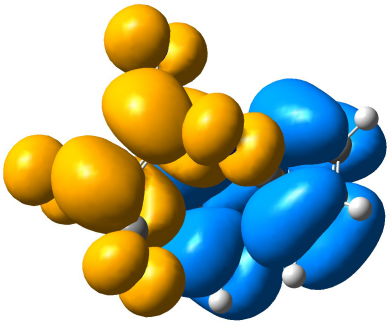


(h) LUMOL+2

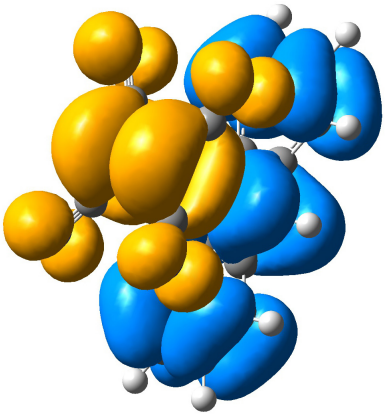
Figure S2: CMOs and orbitalets near FMO(L)s of the DBA CT system: (a) HOMO-2, (b) HOMOL-2, (c) HOMO, (d) HOMOL, (e) LUMO+1, (f) LUMOL+1, (g) LUMO+2, and (h)LUMOL+2. The excitation from HOMOL-1 to LUMOL can explain the CT process. Iso = 0.05.



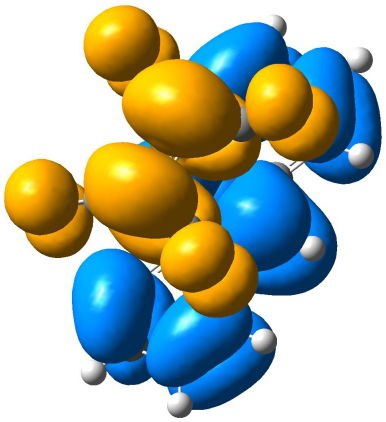
(a) TCNE-benzene



(b) TCNE-naphthalene

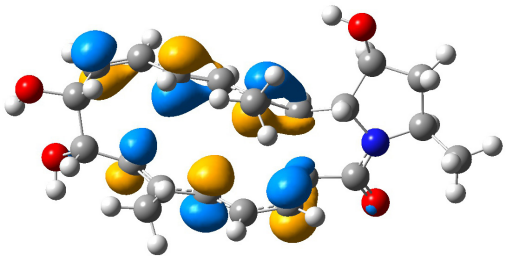


(c) TCNE-anthracene (V)

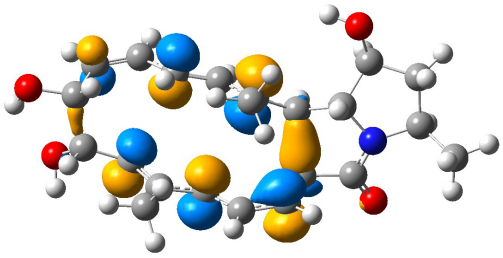


(d) TCNE-anthracene (P)

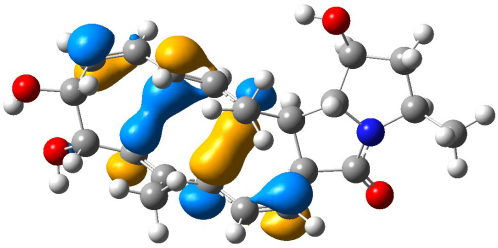
Figure S3: CIS results of the TCNE-aromatic molecule CT systems: (a) TCNE-benzene, (b) TCNE-naphthalene, (c) TCNE-anthracene in V configuration, and (d) TCNE-anthracene in P configuration. CIS calculations show the same CT character as FMOLs do. Iso = 0.02.



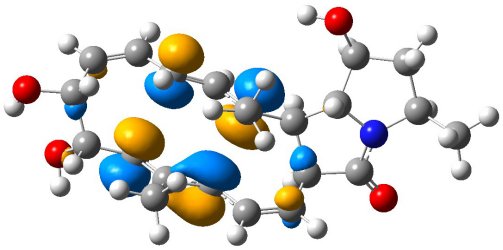
(a) TS1 HOMO



(b) TS1 LUMO

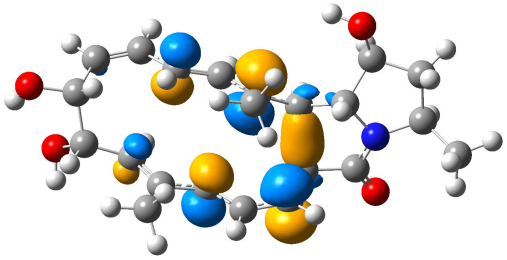


(c) TS2 HOMO

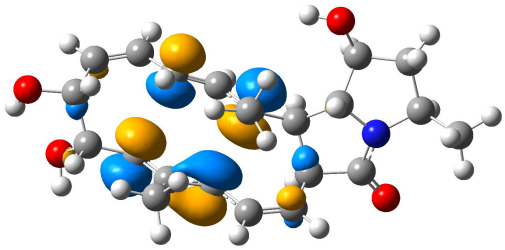


(d) TS2 LUMO

Figure S4: FMOs for TS1 and TS2 of the bifurcating reaction shown in Figure 14: (a) HOMO of TS1, (b) LUMO of TS1, (c) HOMO of TS2, and (d) LUMO of TS2. FMOs cannot clearly explain the bifurcating character of the reaction. Iso = 0.02.

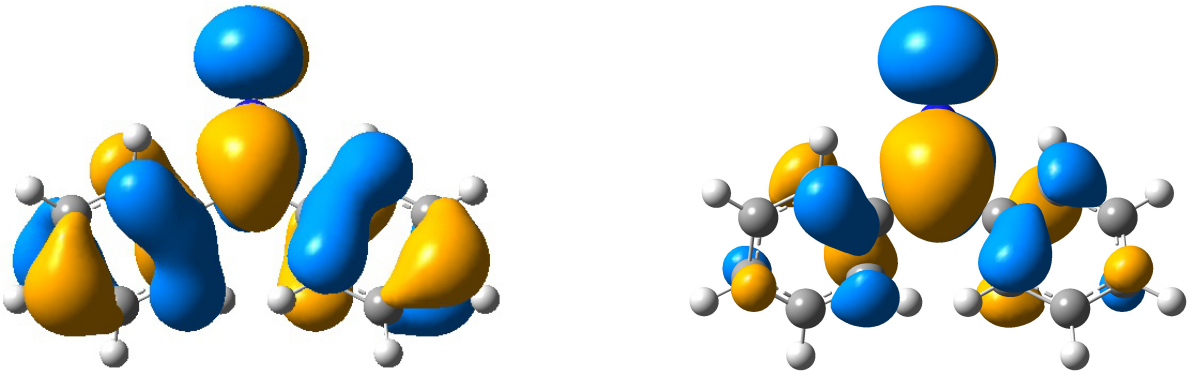


(a) TS1 LUMOL



(b) TS2 LUMOL

Figure S5: LUMOLs for TS1 and TS2 of the bifurcating reaction shown in Figure 14: (a) LUMOL of TS1, (b) LUMOL of TS2. The LUMOLs are mainly localized to the region where the chemical interaction happens.



(a) HOMO (b) LUMO

Figure S6: (a) HOMO and (b) HOMOL of diphenyldiazomethane at Iso = 0.02. Compared to Figure 12 in the main text, using a smaller Iso value can cause each segment of the orbital or orbitalet to be larger, but the overall orbital(et) shapes remain similar.