A Theoretical Study on the Optoelectronic Properties of Merocyanine-Dyes

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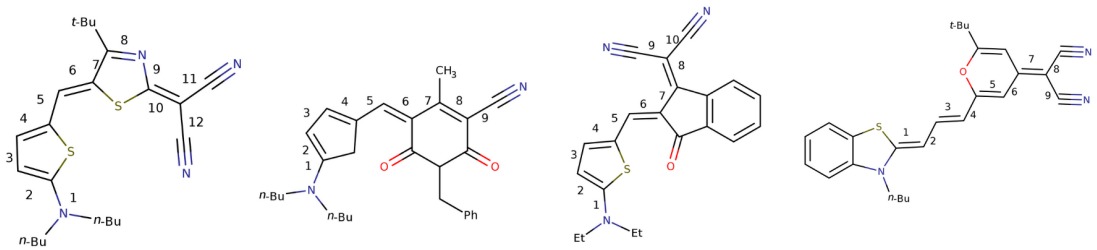


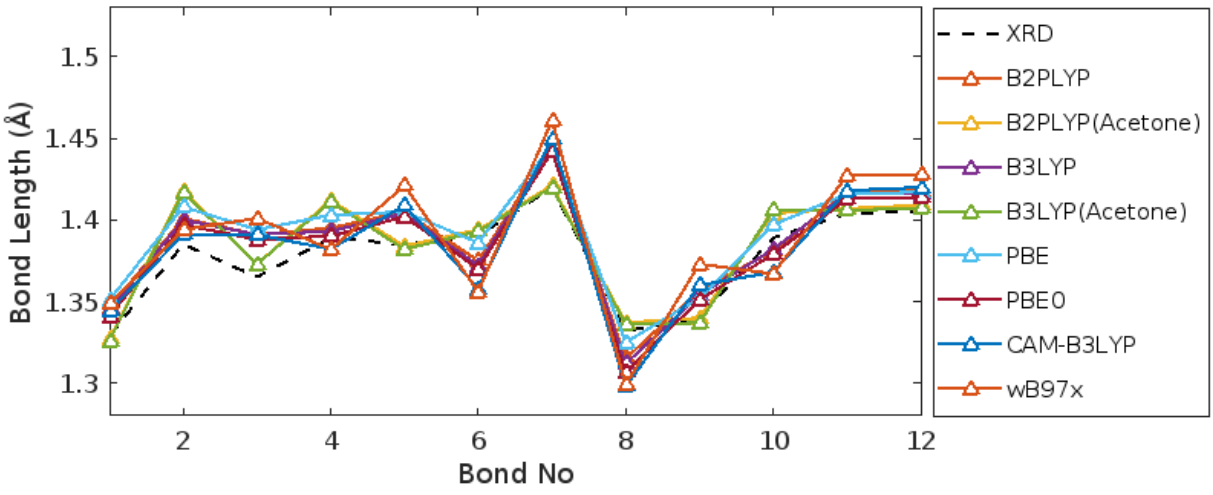
Figure S1: Bond Length alternation paths for merocyanine.

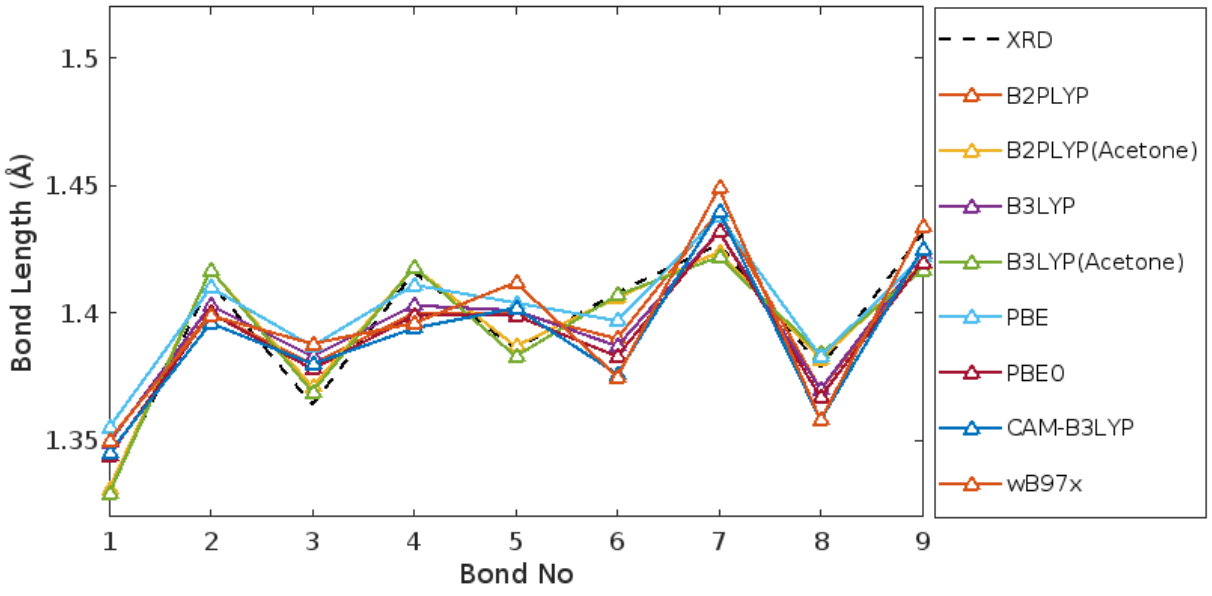
Table S1: Basis-set dependence of the vertical transition energy (eV) of D1A1 calculated with different functionals

Functionals	$S_0 - S_1$ (eV)		
	TZVP	TZVPP	QVZPP
PBE	2.75	2.75	2.74
PBE0	2.87	2.87	2.86
B3LYP	2.84	2.84	2.83
CAM-B3LYP	2.91	2.91	2.90

Table S2: Basis-set dependence of the HOMO energy (eV) of D1A1 calculated with different functionals

Functionals	HOMO(eV)					
	cc-pVDZ			cc-pVTZ		
	G_0W_0	G_6W_0	G_6W_6	G_0W_0	G_6W_0	G_6W_6
PBE	-5.70	-5.79	-5.99	-6.19	-6.38	-6.56
B3LYP	-5.97	-5.97	-6.11	-6.48	-6.55	-6.68
BHLYP	-6.31	-6.28	-6.33	-6.79	-6.81	-6.67


Bond Length (Å)
1.5
1.45
1.4
1.35
1.3
2
4
6
8
10
12
Bond No
XRD
B2PLYP
B2PLYP(Acetone)
B3LYP
B3LYP(Acetone)
PBE
PBE0
CAM-B3LYP
wB97x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1.5
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Bond No
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B3LYP(Acetone)
PBE
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CAM-B3LYP
wB97x

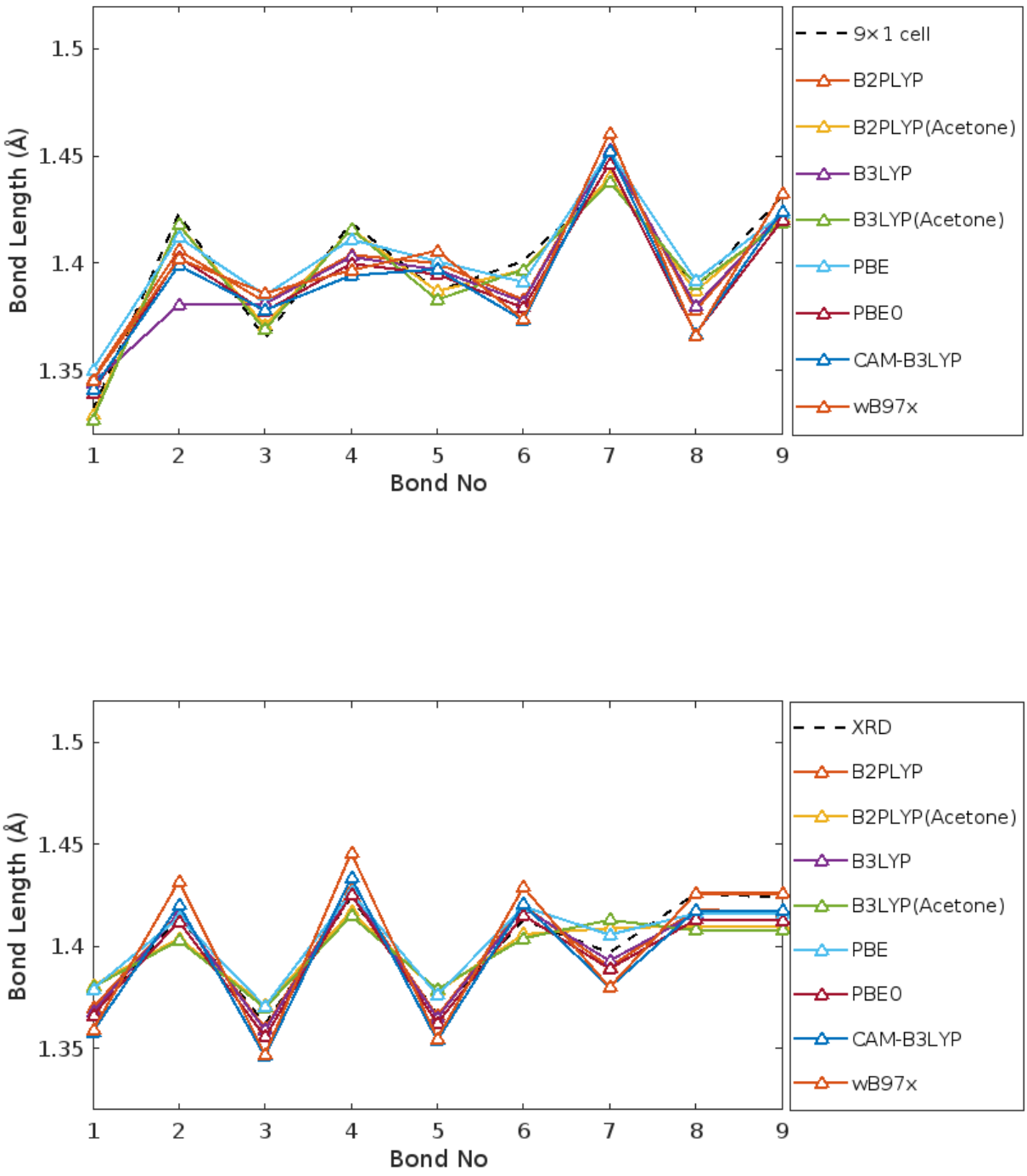

Figure S2: Comparison of the calculated and measured bond length alternations of the merocyanines investigated in this work, namely D1A1, D1A2, D1A3 and D2A4 using B2PLYP, B3LYP, PBE, PBE0, CAM-B3LYP and wB97x for gas phase optimizations and B2PLYP and B3LYP for solvent (acetone) optimizations.

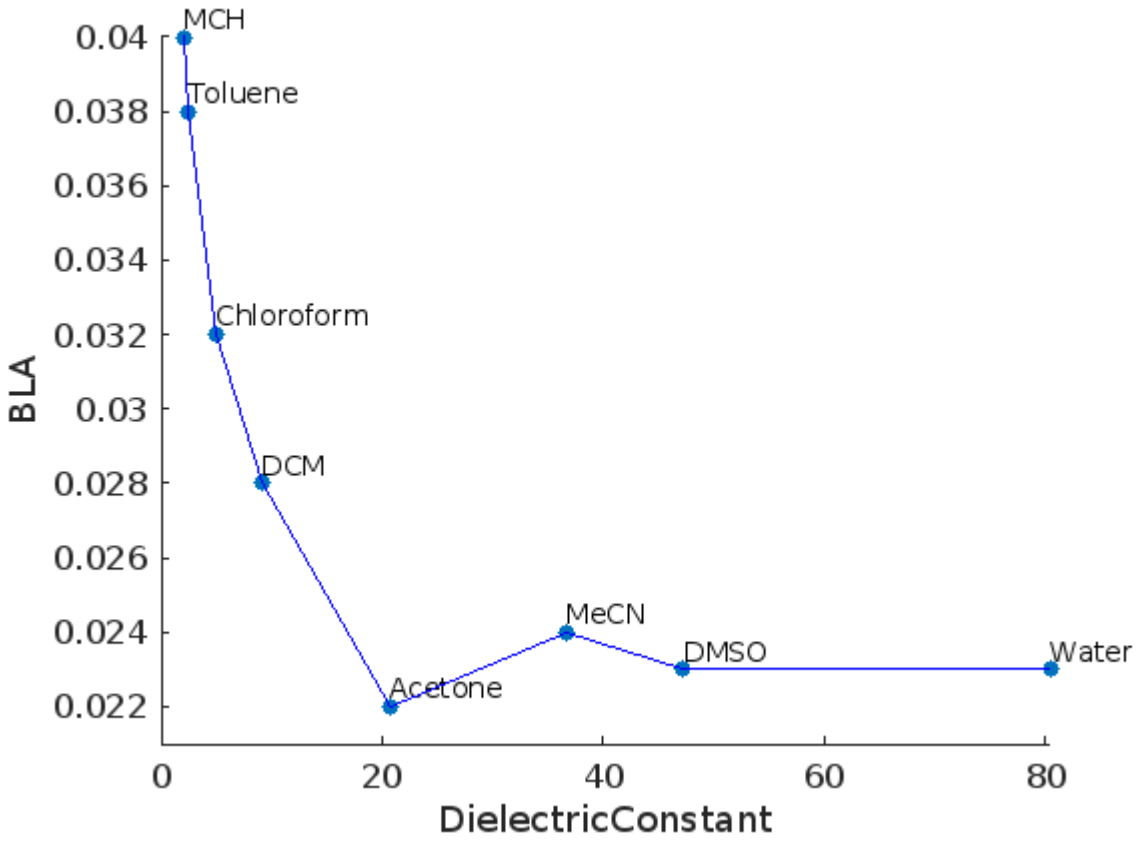

Figure S3: The bond length alternation dependence of MC D2A4 on the dielectric constant of the solution calculated at B2PLYP/D3 level with def2-TZVP basis set. Actual values are represented by circles, solid line serve as guide to the eye.

Table S3: Crystallographic Parameters of MCs including the two different polymorphs of D1A1 namely P1 and P2.

	P1-D1A1[a]	P2-D1A1[b]	D1A2[c]	D1A3[d]	D2A4[e]
Temp. (K)	295	100	100	100	100
CCDC	2073437	2073438	1007699	1406539	1957268
a(Å)	13.09	13.94	8.17	4.96	7.03
b(Å)	19.3	18.85	11.65	13.74	11.04
c(Å)	9.84	9.08	13.66	26.02	15.22
$\alpha(^\circ)$	90	90	107.7	90	76.5
$\beta(^\circ)$	101.7	105.6	102.1	93.3	89.7
$\gamma(^\circ)$	90	90	96.2	90	78.3
Z	4	4	2	4	2
Space Group	$P21/c$	$P21/c$	$P-1$	$P21/n$	$P-1$

[a]:Reference[1]; [b]:Reference[1]; [c]:Reference[2]; [d]:Reference[3]; [e]:Reference[4];

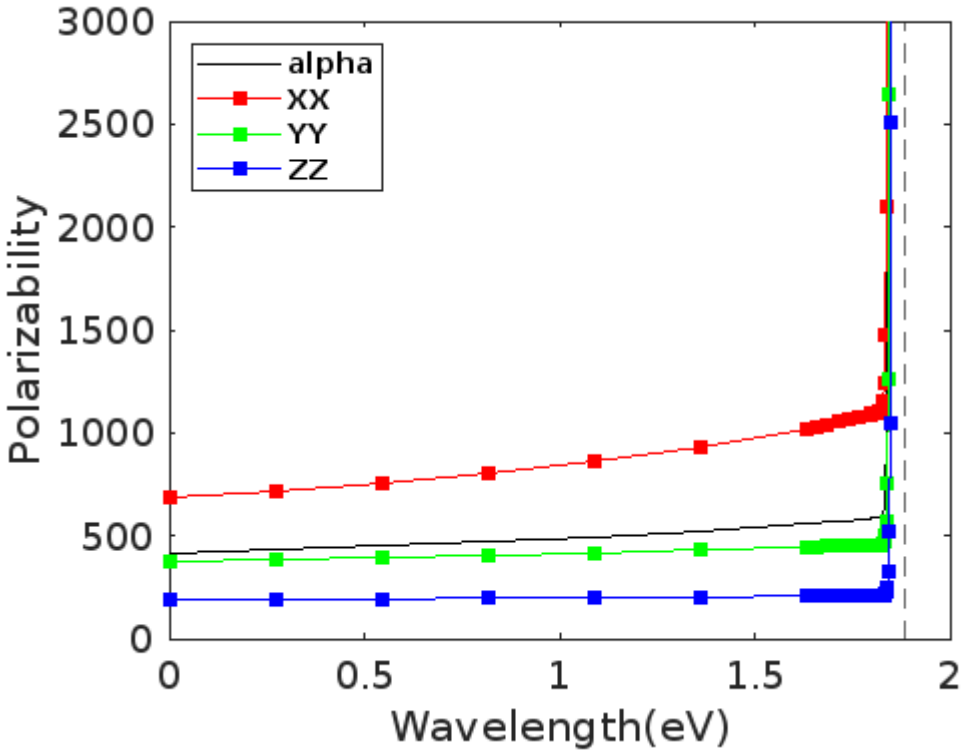

Figure S4: The energy dependence of the many-body polarizability tensor for **D1A1** merocyanine molecule in gas phase computed using TDCP-B3LYP. Actual values are represented by squares, dashed lines serve as visual cues. The dashed lines represent the optical gap of the molecule.

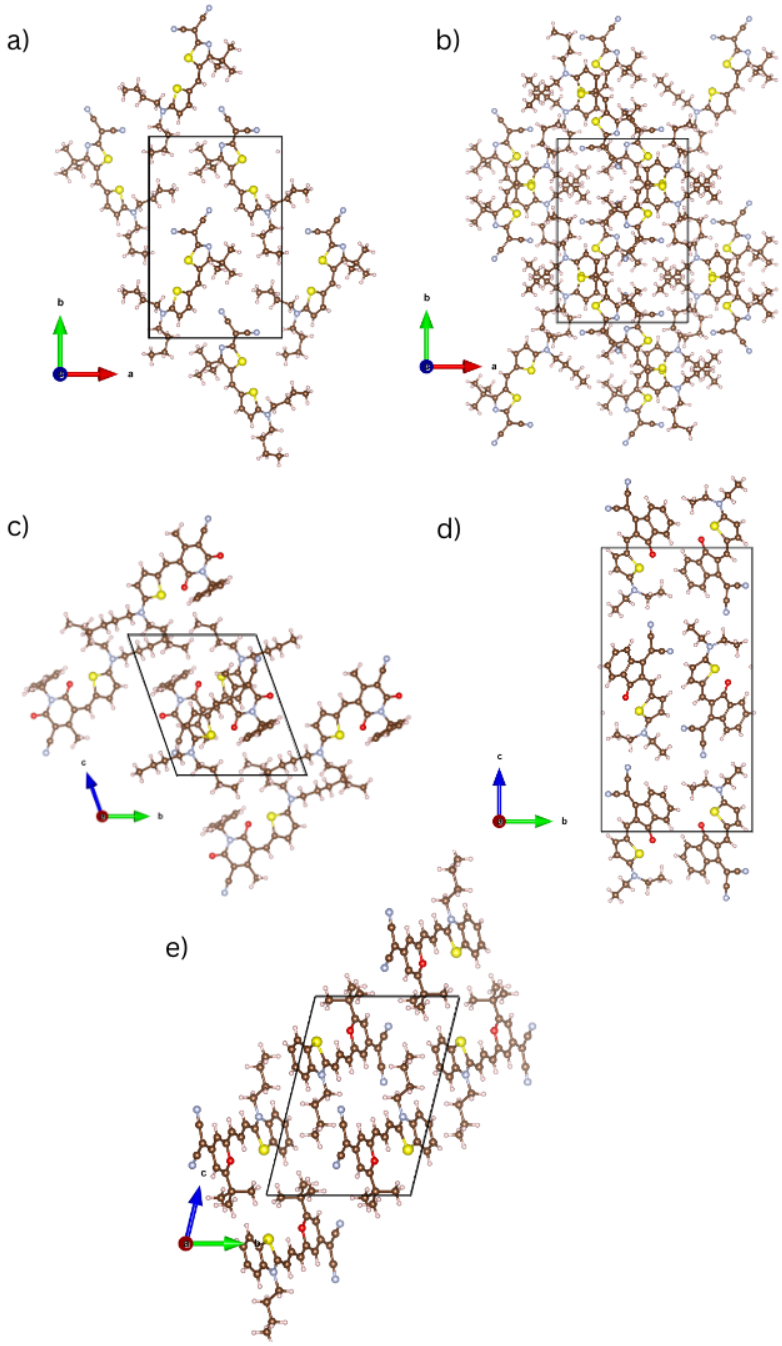

Figure S5: The molecular crystal structures of D1A1 polymorphs a) P1-D1A1, b)P2-D1A1 and merocyanines c) D1A2, d) D1A3 and d) D2A4.

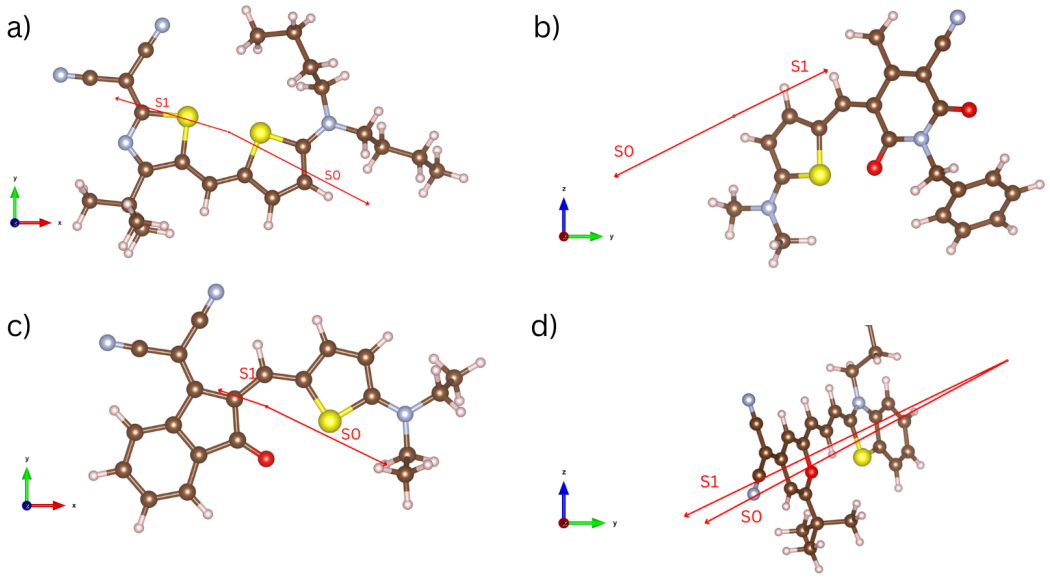

Figure S6: Transition dipole moment vectors for the ground state (S_0) and first excited state(S_1) calculated using TD-DFT at PBE-D3/def2-TZVPP level of merocyanines: a) D1A1, b) D1A2, c) D1A3 and d) D2A4.

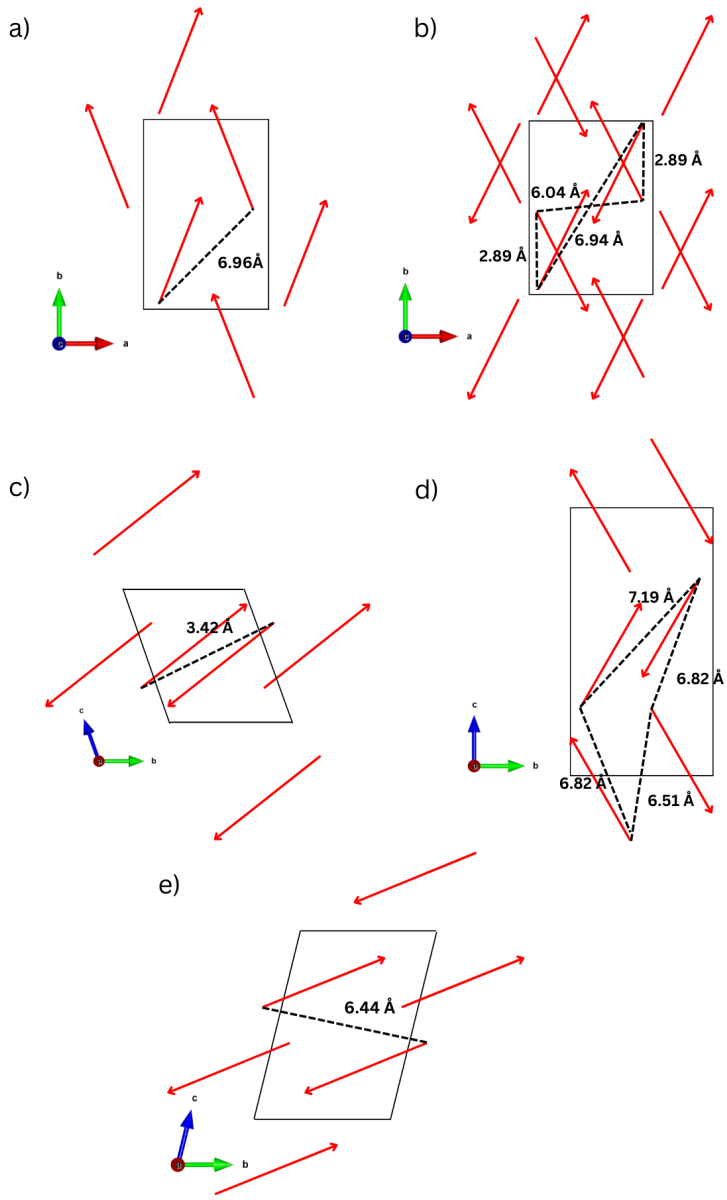

Figure S7: Representative picture of the excited state transition dipole moment for the crystal structures given in Figure S4. The red arrows represent the direction of transition dipole moment vectors of each molecular unit the crystal structure of the respective merocyanines and the black dotted lines represent the distance between the barycentre of adjacent molecules.

References

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