

Supporting Information

Dimer geometry

The following table gives the coordinates of the *trans* TF-Az-OMe dimer at a distance $R = 7.8 \text{ \AA}$, with monomer coordinates optimized for the S_0 state on the B3LYP/6-31G* level of theory.

atom	x	y	z	atom	x	y	z
atom	x	y	z				
C	-1.703854	2.356859	-6.631330	C	-1.703854	-5.443141	-6.631330
C	-0.654184	2.534540	-5.722633	C	-0.654184	-5.265460	-5.722633
C	0.424212	3.374367	-6.074178	C	0.424212	-4.425633	-6.074178
C	0.436365	4.009534	-7.300044	C	0.436365	-3.790466	-7.300044
C	-0.625552	3.825703	-8.209851	C	-0.625552	-3.974297	-8.209851
C	-1.701102	2.993849	-7.870478	C	-1.701102	-4.806151	-7.870478
N	-0.772803	1.837611	-4.505097	N	-0.772803	-5.962389	-4.505097
N	0.177104	2.014133	-3.690800	N	0.177104	-5.785867	-3.690800
C	0.044849	1.301472	-2.471707	C	0.044849	-6.498528	-2.471707
C	1.074842	1.501344	-1.543075	C	1.074842	-6.298656	-1.543075
C	1.050320	0.852502	-0.312272	C	1.050320	-6.947498	-0.312272
C	-0.008693	-0.004211	-0.002442	C	-0.008693	-7.804211	-0.002442
C	-1.042349	-0.207973	-0.927327	C	-1.042349	-8.007973	-0.927327
C	-1.019707	0.439737	-2.154726	C	-1.019707	-7.360263	-2.154726
C	-0.008693	-0.756210	1.300058	C	-0.008693	-8.556210	1.300058
F	0.610319	-1.955661	1.185214	F	0.610319	-9.755661	1.185214
O	-0.508222	4.498168	-9.383646	O	-0.508222	-3.301832	-9.383646
C	-1.539756	4.361743	-10.352220	C	-1.539756	-3.438257	-10.352220
F	0.635491	-0.076677	2.275317	F	0.635491	-7.876677	2.275317
F	-1.262794	-1.005905	1.739357	F	-1.262794	-8.805905	1.739357
H	-2.525501	1.707126	-6.345508	H	-2.525501	-6.092874	-6.345508
H	-2.526901	2.838973	-8.554799	H	-2.526901	-4.961027	-8.554799
H	1.255070	4.659675	-7.592600	H	1.255070	-3.140325	-7.592600
H	1.234967	3.507735	-5.366851	H	1.234967	-4.292265	-5.366851
H	1.884275	2.174071	-1.808293	H	1.884275	-5.625929	-1.808293
H	1.844750	1.013938	0.408581	H	1.844750	-6.786062	0.408581
H	-1.864974	-0.869781	-0.675746	H	-1.864974	-8.669781	-0.675746
H	-1.812104	0.297056	-2.880367	H	-1.812104	-7.502944	-2.880367
H	-1.645378	3.320043	-10.680705	H	-1.645378	-4.479957	-10.680705
H	-2.502128	4.720493	-9.965694	H	-2.502128	-3.079507	-9.965694
H	-1.236238	4.979608	-11.198701	H	-1.236238	-2.820392	-11.198701

Table 1: Cartesian coordinates of the TF-Az-OMe dimer at intermolecular distance of 7.8 Å. The optimized structure of the monomers was used.

Lowest-energy $\pi \rightarrow \pi^*$ transition

The lowest-energy $\pi \rightarrow \pi^*$ transition in TF-Az-OMe is dominated by a HOMO \rightarrow LUMO excitation. The frontier orbitals are schematically indicated in the following figure.

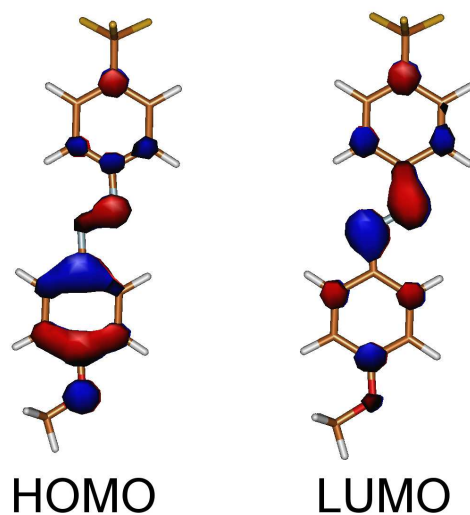


Figure 1: Kohn-Sham frontier orbitals HOMO and LUMO of the monomer (B3LYP/6-31G*), which dominate the strongest $\pi \rightarrow \pi^*$ transition according to TD-B3LYP/6-31G*.

TD-DFT calculations for the dimer

distance R [Å]	transition	ΔE_{eg} [eV]	μ_{eg} [ea ₀]	character
3.5	$S_0 \rightarrow S_4$	2.860	1.36	$\pi \rightarrow \pi^*$
	$S_0 \rightarrow S_8$	3.342	2.09	mix. $\rightarrow \pi^*$
	$S_0 \rightarrow S_9$	3.451	1.73	mix. $\rightarrow \pi^*$
	$S_0 \rightarrow S_{12}$	3.886	2.36	$\pi \rightarrow \pi^*$
4.0	$S_0 \rightarrow S_6$	3.417	1.67	mix. $\rightarrow \pi^*$
	$S_0 \rightarrow S_7$	3.492	2.12	mix $\rightarrow \pi^*$
	$S_0 \rightarrow S_8$	3.554	2.43	mix. $\rightarrow \pi^*$
4.5	$S_0 \rightarrow S_9$	3.671	1.70	$\pi \rightarrow \pi^*$
	$S_0 \rightarrow S_8$	3.587	4.20	$\pi \rightarrow \pi^*$
	$S_0 \rightarrow S_8$	3.581	4.38	$\pi \rightarrow \pi^*$
5.0	$S_0 \rightarrow S_8$	3.569	4.45	$\pi \rightarrow \pi^*$
5.5	$S_0 \rightarrow S_8$	3.557	4.50	$\pi \rightarrow \pi^*$
6.0	$S_0 \rightarrow S_8$	3.546	4.53	$\pi \rightarrow \pi^*$
6.5	$S_0 \rightarrow S_7$	3.537	4.56	$\pi \rightarrow \pi^*$
7.0	$S_0 \rightarrow S_7$	3.530	4.58	$\pi \rightarrow \pi^*$
7.5	$S_0 \rightarrow S_7$	3.523	4.61	$\pi \rightarrow \pi^*$
8.0	$S_0 \rightarrow S_6$	3.517	4.62	$\pi \rightarrow \pi^*$
8.5	$S_0 \rightarrow S_6$	3.513	4.64	$\pi \rightarrow \pi^*$
9.0	$S_0 \rightarrow S_6$	3.508	4.65	$\pi \rightarrow \pi^*$
9.5	$S_0 \rightarrow S_6$	3.505	4.66	$\pi \rightarrow \pi^*$
10.0	$S_0 \rightarrow S_6$	3.477	3.37	$\pi \rightarrow \pi^*$
monomer	$S_0 \rightarrow S_2$			

Table 2: Excitation energies, transition dipole moments, and characters of the strongest transitions for different intermolecular distances in the dimer model, obtained with TD-B3LYP/6-31G*. By “mix.” we indicate mixed n - and π -character.

A simple, Hückel-type excitonic band model

If $N = 2M + 1$ are placed along a chain with periodic boundary conditions, assuming that nearest neighbours (only) at distance R interact through a coupling matrix element $\Delta^{(2)}$, the single-exciton states form a band with energies given by Eq.(14), and corresponding single-exciton wavefunctions given by

$$\psi(k) = \frac{1}{\sqrt{N}} \sum_{n=-M}^{+M} e^{iknR} \Phi_n \quad , \quad (1)$$

where $|\Phi_n\rangle = |gg \cdots geg \cdots gg\rangle$ has an excitation (e) at the n -th position of the chain. In the ground state ψ_G , which is assumed to be a dispersionless product state, all monomers are unexcited. The transition dipole matrix

elements for transitions from the ground state into the single-exciton band are

$$\underline{\mu}_G(k) = \langle \psi_G | \hat{\underline{\mu}} | \psi(k) \rangle \quad (2)$$

$$= \langle gg \cdots g | \sum_{m=-M}^{+M} \hat{\underline{\mu}}^{(m)} | \frac{1}{\sqrt{N}} \sum_{n=-M}^{+M} e^{iknR} gg \cdots geg \cdots gg \rangle \quad (3)$$

$$= \frac{1}{\sqrt{N}} \sum_{n=-M}^{+M} e^{iknR} \underline{\mu}_{eg}^{(n)} \quad , \quad (4)$$

where $\underline{\mu}_{eg}^{(n)}$ is the transition dipole of the n -th monomer. The strongest total transition dipole moment occurs for $k = 0$ and is given by Eq.(15).