Electronic Supplementary Information for

Narrowband emission from fully bridged triphenylamine derivatives: Insight into effects of structure modification and pressure

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1. Definition of RMSD

The root mean square displacement (RMSD) is a simple and versatile metric to quantitatively measure the overall structural changes among different geometries. For a given molecule with N atoms, the RMSD value can be evaluated as

$$RMSD = \sqrt{\frac{1}{N}\sum_{i}^{natom}\left[(x_i - x_i^{'})^2 + (y_i - y_i^{'})^2 + (z_i - z_i^{'})^2\right]}$$

where x_i and $x_i^{'}$ are the *x*-coordinates of the ith atom in the first and second geometry, respectively, as are *y* and *z*.

2. Definitions of MPP and SDP

For a given molecule with N atoms, the molecular planarity parameter (MPP) can be defined as the root-mean-square of deviation of atoms from the fitting plane

$$MPP = \sqrt{\frac{1}{N}\sum_i d_i^2}$$

where d_i is the distance between the atom *i* and the fitting plane. The signed distance between the atom *i* and the fitting plane can be evaluated as

$$d_i^s = \frac{Ax_i + By_i + Cz_i + D}{\sqrt{A^2 + B^2 + C^2}}$$

where *A*, *B*, *C*, *D* are parameters of the fitting plane. Following that, the span of deviation from plane (SDP) can be defined as

$$SDP = d_{\max}^s - d_{\min}^s$$

where the $d_{\max}^s$ and $d_{\min}^s$ are the most positive and the most negative d^s values among all the considered atoms, respectively.

3. Definitions of *D* and S_r indexs

The charge transfer length in the X/Y/Z direction can be simulated by evaluating the distance between the centroid of hole and electron in the corresponding directions:

$$D_x = \left|X_{\text{ele}} - X_{\text{hole}}\right|, D_y = \left|Y_{\text{ele}} - Y_{\text{hole}}\right|, D_z = \left|Z_{\text{ele}} - Z_{\text{hole}}\right|$$

According to abovementioned definitions, the total magnitude of the charge transfer length can be defined as *D* index:

$$D = \sqrt{(D_x)^2 + (D_y)^2 + (D_z)^2}$$

The overlap function between the hole and electron distribution can be defined as

$$S_r(r) = \sqrt{\rho^{\text{hole}}(r)\rho^{\text{ele}}(r)}$$

in which ρ^{hole} and ρ^{ele} are the density distribution of hole and electron, respectively. The S_r index means the overlapping extent of the hole and electron, and it can be defined as the integral of the S_r function:

$$S_r = \int S_r(r)dr = \sqrt{\rho^{\text{hole}}(r)\rho^{\text{ele}}(r)}$$

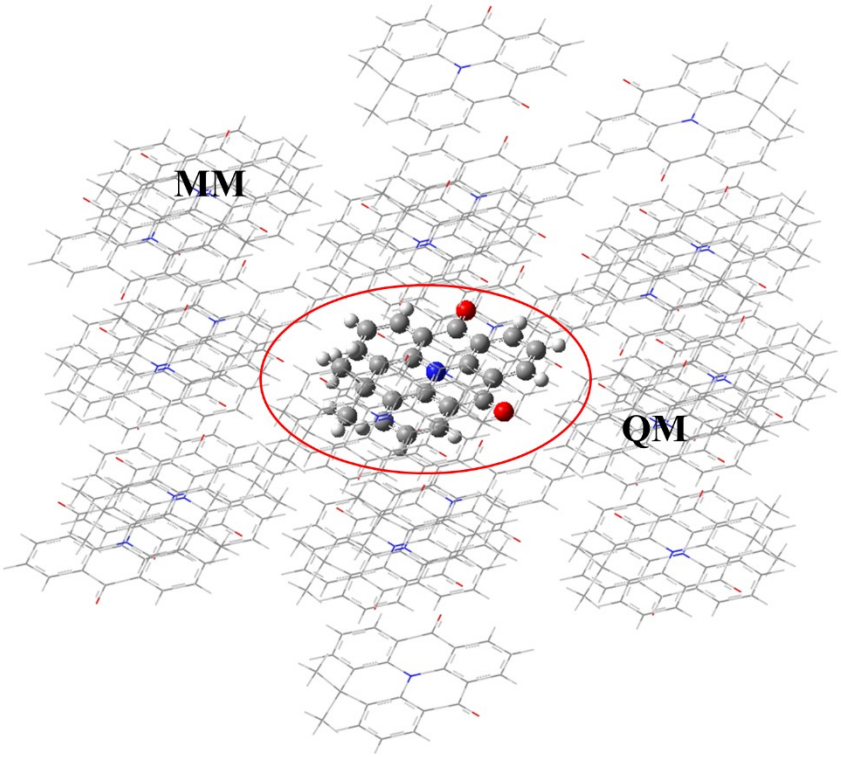

Fig. S1 Two-layered ONIOM model of DQAO in the aggregated state.

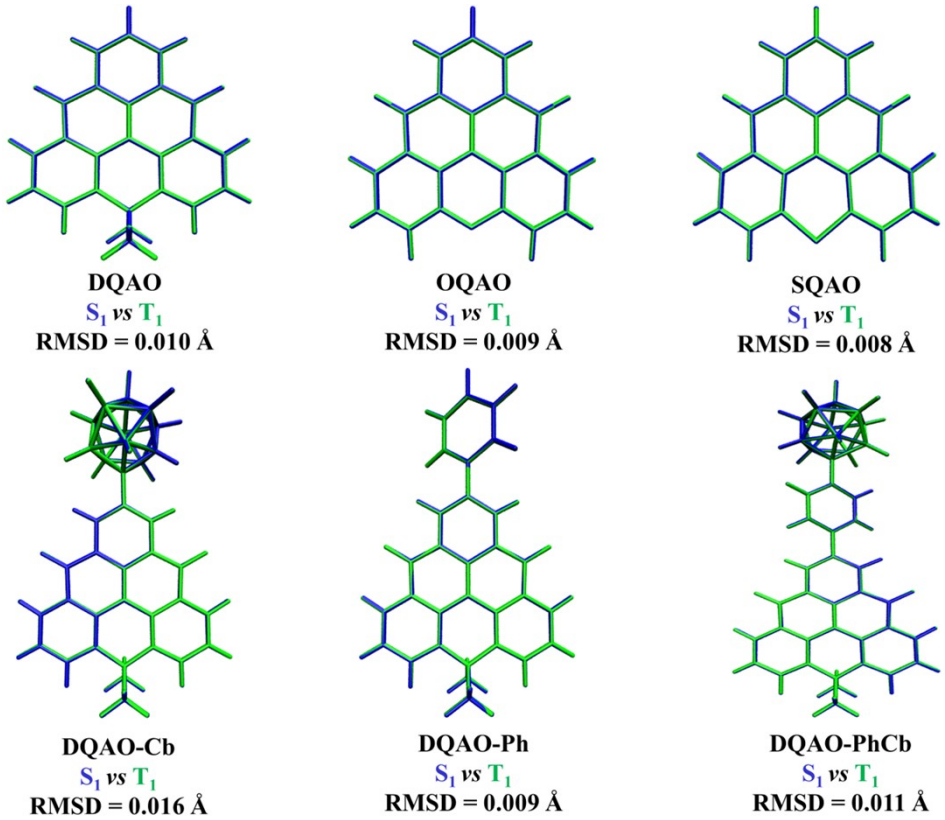

Fig. S2. Geometry comparisons and RMSD values for the S_1 (blue) *vs* T_1 (green) of all the systems considered here.

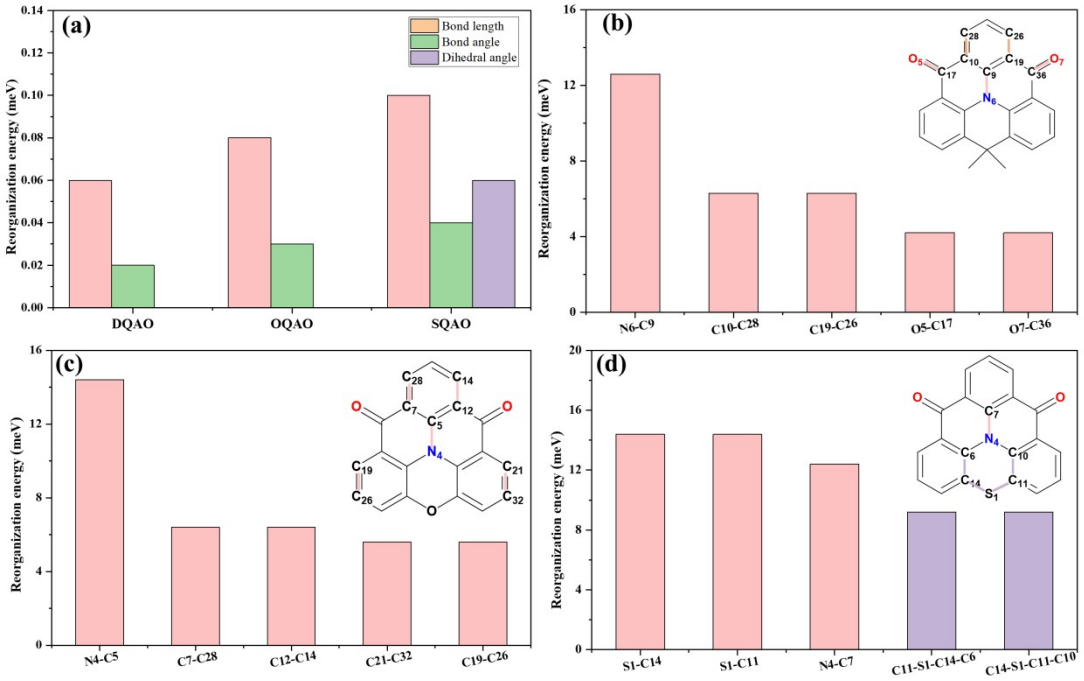

Fig. S3 Contributions of bond lengths, bond angles, and dihedral angles to the reorganization energies between S_0 and S_1 at S_1-optimized geometries (a) for DQAO (b), OQAO (c), SQAO (d), respectively (shown with the largest five contributions).

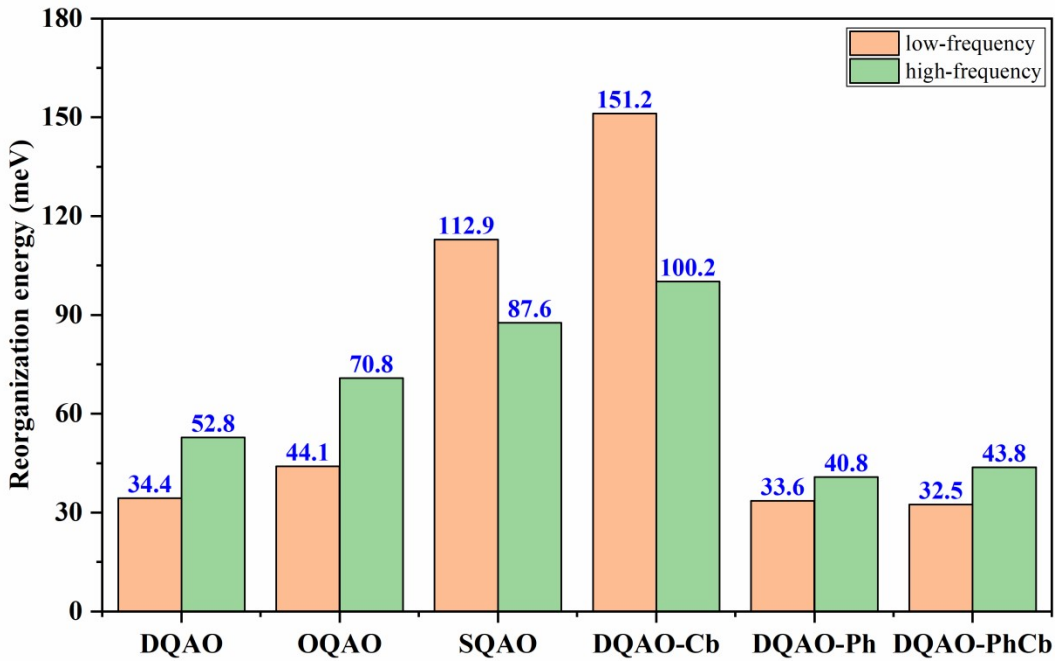

Fig. S4 Contributions of low-frequency vibrations (< 1000 cm^{-1}) and high-frequency vibrations (≥ 1000 cm^{-1}) to the reorganization energies of all the studied systems.

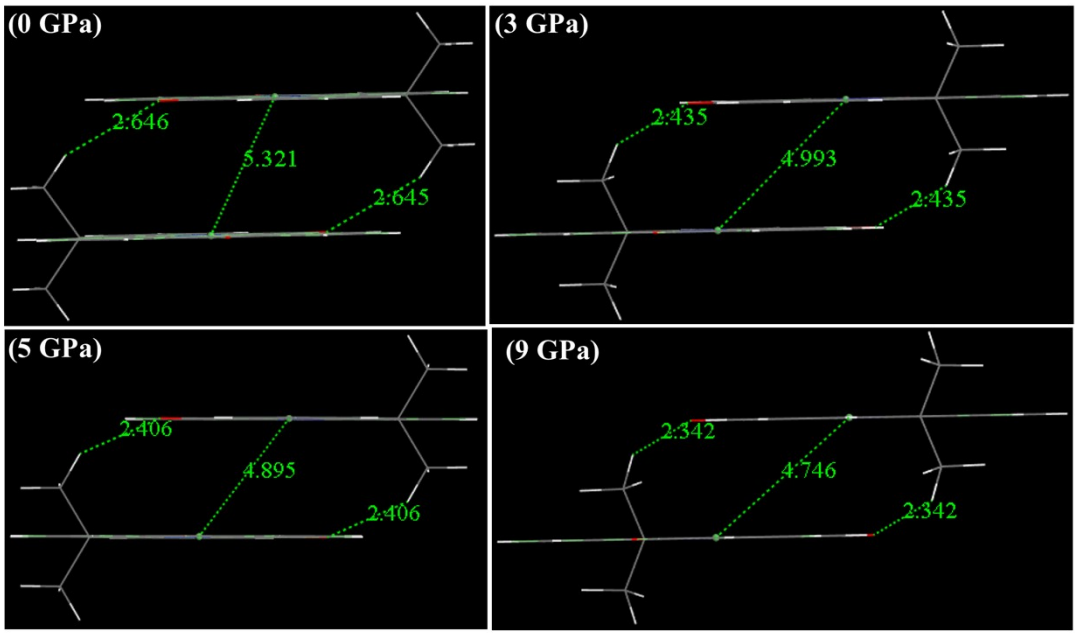

Fig. S5 Centroid distances of π-stacked dimers extracted from the DQAO unit cell at various external pressures, where units are in Å.

Table S1. Emission energies of S_1 and T_1 (eV), the maximum wavelength of fluorescence (λ_{emi}, nm), and S_1-T_1 energy gaps (ΔE_{ST}, eV) simulated by combining B3LYP, PBE0, MN15, and wb97xd functionals with def-TZVP basis sets, respectively, as well as the λ_{emi} and ΔE_{ST} values obtained in the experiment.[15]

		B3LYP	PBE0	MN15	CAM-B3LYP	Expt.
DQAO	S_1	2.74	2.86	3.09	3.28	2.66
	λ_{emi}	452	434	401	378	465
	T_1	2.28	2.32	2.53	2.54	2.47
	ΔE_{ST}	0.46	0.53	0.56	0.75	0.19
OQAO	S_1	2.35	2.47	2.73	2.92	2.34
	λ_{emi}	528	503	454	425	520
	T_1	1.96	2.02	2.28	2.31	2.18
	ΔE_{ST}	0.39	0.45	0.46	0.60	0.16
SQAO	S_1	2.16	2.29	2.62	2.83	2.23
	λ_{emi}	573	541	474	439	552
	T_1	1.86	1.94	2.25	2.33	2.07
	ΔE_{ST}	0.30	0.35	0.37	0.50	0.16

Table S2. Calculated vertical excitation energies of S_1 (ΔE_{S1}, eV) and T_1 (ΔE_{T1}, eV), fluorescence peaks (λ_{emi}, nm), and energy gaps between S_1 and T_1(ΔE_{ST}, eV) by the wavefunction-based STEOM-DLPNO-CCSD/def2-SVP calculations, together with the fluorescence peaks (λ_{expt}, nm) and energy gaps between S_1 and T_1 (ΔE_{expt}, eV) measured in experiment.

	DQAO	**OQAO**	**SQAO**
S_1	2.96	2.65	2.62
λ_{emi}	419	469	474
T_1	2.68	2.43	2.43
ΔE_{ST}	0.28	0.22	0.18
λ_{expt}	465	520	552
ΔE_{expt}	0.19	0.16	0.16

Table S3. The lattice parameters of the DQAO unit cell at ambient pressure and various external pressures of 3, 5, and 7 Gpa, respectively.

	a (Å)	*b* (Å)	*c* (Å)	Density (g/cm^3)	Volume (Å^3)	|R/D|
0 GPa	22.78	6.78	11.55	1.35	1661.83	0.42
3 GPa	21.64	6.26	10.93	1.62	1385.04	0.72
5 GPa	21.48	6.09	10.80	1.70	1315.21	0.83
9 GPa	21.22	5.85	10.63	1.83	1221.74	1.05

Table S4. Interaction energy decomposition of the π-stacked dimers of DQAO calculated by the EDA-FF approach at various external pressures, where energies are in kJ/mol.

	electrostatic	repulsion	dispersion	total
0 GPa	-5.67	52.81	-126.55	-79.41
3 GPa	-6.61	134.82	-187.79	-59.58
5 GPa	-6.85	177.66	-212.92	-42.11
9 GPa	-7.22	270.79	-256.99	6.59

Table S5. Contribution of each non-hydrogen atom to hole and electron of the reported DQAO and its structure-modified derivatives DQAO-Cb, DQAO-Ph, and DQAO-PhCb.

Atoms	DQAO		DQAO-Cb		DQAO-Ph		DQAO-PhCb	
	Hole (%)	Electron (%)	Hole (%)	Electron (%)	Hole (%)	Electron (%)	Hole (%)	Electron (%)
C1	1.52	0.03	1.59	0.03	1.31	0.03	1.40	0.03
O5	3.86	8.17	3.64	7.79	3.68	8.21	3.72	8.15

N6	19.85	0.05	19.34	0.04	17.32	0.06	18.63	0.05
O7	3.86	8.17	3.55	8.28	3.67	8.21	3.72	8.17
C8	3.52	2.78	4.06	2.34	2.10	2.83	2.91	2.69
C9	0.18	0.35	0.16	0.24	1.04	0.37	0.39	0.28
C10	3.86	4.02	3.52	5.30	4.33	3.83	4.03	4.29
C11	3.52	2.78	3.75	2.52	2.10	2.83	2.90	2.68
C12	3.03	1.29	2.96	0.83	2.32	1.38	2.64	1.18
C13	0.26	3.56	0.24	2.88	0.37	3.76	0.34	3.48
C15	8.72	0.26	9.02	0.16	6.98	0.28	8.03	0.23
C16	8.72	0.26	8.84	0.20	6.98	0.28	8.03	0.24
C17	0.76	8.62	0.72	7.78	0.82	8.76	0.79	8.57
C18	3.03	1.29	2.82	0.89	2.32	1.38	2.63	1.17
C19	3.86	4.02	3.47	5.22	4.33	3.83	4.04	4.31
C20	7.69	0.23	8.06	0.14	5.73	0.24	6.79	0.19
C22	0.26	3.56	0.25	3.20	0.37	3.75	0.34	3.47
C24	3.54	3.08	3.82	2.58	3.03	3.23	3.44	3.04
C26	0.40	17.39	0.21	18.36	1.57	16.51	0.78	17.16
C28	0.40	17.39	0.18	17.61	1.57	16.51	0.78	17.18
C30	3.54	3.08	3.75	2.92	3.03	3.23	3.44	3.05
C32	7.69	0.23	7.71	0.14	5.73	0.24	6.78	0.19
C34	3.78	0.46	3.20	0.49	5.67	0.47	4.58	0.46
C36	0.76	8.62	0.76	8.58	0.82	8.76	0.79	8.60
C37	0.76	0.00	0.83	0.00	0.58	0.00	0.70	0.00
C38	1.73	0.03	1.85	0.02	1.19	0.03	1.57	0.03
C41	-	-	-	-	2.07	0.06	0.63	0.10
C42	-	-	-	-	2.12	0.11	1.16	0.14
C43	-	-	-	-	2.12	0.11	1.19	0.12
C44	-	-	-	-	0.33	0.08	0.08	0.07
C46	-	-	-	-	0.33	0.08	0.08	0.09
C48	-	-	-	-	3.30	0.03	1.49	0.05
C	-	-	0.06	0.02	-	-	0.03	0.01
C	-	-	0.02	0.05	-	-	0.06	0.00
B	-	-	0.11	0.27	-	-	0.02	0.00
B	-	-	0.07	0.01	-	-	0.03	0.00
B	-	-	0.07	0.05	-	-	0.01	0.00
B	-	-	0.13	0.05	-	-	0.01	0.00
B	-	-	0.09	0.21	-	-	0.02	0.00
B	-	-	0.03	0.12	-	-	0.05	0.00
B	-	-	0.03	0.07	-	-	0.04	0.00
B	-	-	0.02	0.08	-	-	0.03	0.00
B	-	-	0.06	0.04	-	-	0.03	0.00
B	-	-	0.09	0.08	-	-	0.01	0.00