Supporting Information

Hybridization and De-hybridization between Locally-excited (LE) state and Charge-transfer (CT) state: A Combined Experimental and Theoretical Study

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Contents

SI-1: Functional Selection

Three DFT functional (B3lyp, M062x and ωb97xd) are used to choose the most suitable functional. B3lyp, which has a well-known problem, is obviously underestimated CT state enenrgy. Compared the simulation data with the emitting wavelengths of TPMCN and TPBMCN, M062x is the closest to the Experimental data. So we choose M062x for the following calculation. The NTOs and emiting wavelengths of H_1V_2 in acetonitrile were calculated by using the polarizable continuum model (PCM) under M062x functional and 6-31G(d,p) basis set.

Table S1 Emiting wavelengths of TPMCN and TPBMCN in Experiment and various TD-DFT(B3lyp, M062x and ωb97xd)

	molecule	TD-B3lyp (nm)	TD-M062x (nm)	TD-ωb97xd (nm)	Experiment (nm)
TPMCN	Absorption	482	341	363	360
	Emission	654	444	487	440
TPBMCN	Absorption	461	331	365	364
	Emission	615	406	472	415

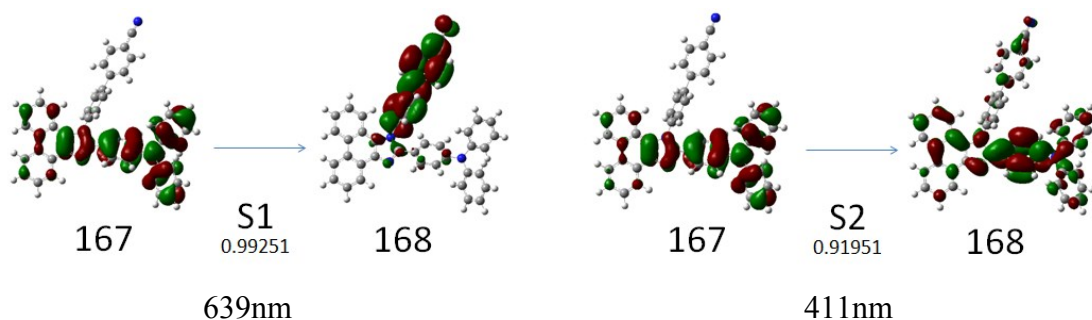Figure S1 NTOs on S0-geometry and calculated emiting wavelengths of S1 and S2 states of H1V2 in acetonitrile

SI-2: Computational methodology

Solvatochromic effect

The influence of solvent environment on the optical property of our compounds can be understood using the Lippert-Mataga equation, a model that describes the interactions between the solvent and the dipole moment of solute:

$$hc(v_a - v_f) = hc(v_a^0 - v_f^0) - \frac{2(\mu_e - \mu_g)^2}{a^3} f(\varepsilon, n)$$

where f is the orientational polarizability of the solvent, $v_a^0 - v_f^0$ corresponds to the Stokes shifts when f is zero, μ_e is the excited state dipole moment, μ_g is the ground-state dipole moment; a is the solvent cavity (Onsager) radius, derived from the Avogadro number (N), molecular weight (M), and density (d=1.0 g/cm^3); ε and n are the solvent dielectric and the solvent refractive index, respectively; $f(\varepsilon,n)$ and a can be calculated respectively as follows:

$$f(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}, \ a = (3M/4N\pi d)^{1/3}$$

Centroids of charge[SI-1]

The points in spaces where an increment or a depletion of the density upon absorption is produced is defined as:

$$
\rho_+(r) = \begin{cases} \rho_{EX}(r) - \rho_{GS}(r) & if \quad \rho_{EX}(r) > \rho_{GS}(r) \\ 0 & if \quad \rho_{EX}(r) < \rho_{GS}(r) \end{cases}
$$

$$
\rho_-(r) = \begin{cases} \rho_{EX}(r) - \rho_{GS}(r) & if \quad \rho_{EX}(r) < \rho_{GS}(r) \\ 0 & if \quad \rho_{EX}(r) > \rho_{GS}(r) \end{cases}
$$

(1)

In the equations above, $\rho_{EX}(r)$, $\rho_{GS}(r)$ are the electronic densities associated to the ground and excited states. Therefore two functions (x_+, y_+, z_+), (x_-, y_-, z_-), defining the barycenters of $\rho_+(r)$ and $\rho_-(r)$ is defined as:

$$(x_+, y_+, z_+) = \frac{\int r\rho_+(\mathrm{r})\mathrm{d}r}{\int \rho_+(\mathrm{r})\mathrm{d}r}$$

$$(x_-, y_-, z_-) = \frac{\int r\rho_-(\mathrm{r})\mathrm{d}r}{\int \rho_-(\mathrm{r})\mathrm{d}r}$$

(2)

Also we can get the root-mean-square deviations along the three axes using the equations as below (σ_{aj}, j=x, y, z; a= + or -):

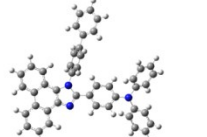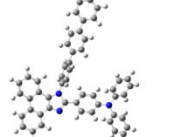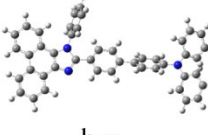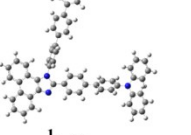$$\sigma_{a,j} = \sqrt{\frac{\sum_i \rho_a(r_i)(j_i - j_a)^2}{\sum_i \rho_a(r_i)}}$$

(3)
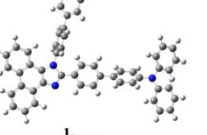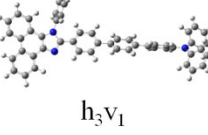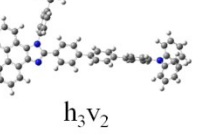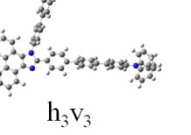
According all the equations above, the centroids of charge can be defined as:

$$C_+(r) = A_+ e\left(-\frac{(x-x_+)^2}{2\sigma^2_{+x}} - \frac{(y-y_+)^2}{2\sigma^2_{+y}} - \frac{(z-z_+)^2}{2\sigma^2_{+z}} \right)$$

$$C_-(r) = A_- e\left(-\frac{(x-x_-)^2}{2\sigma^2_{-x}} - \frac{(y-y_-)^2}{2\sigma^2_{-y}} - \frac{(z-z_-)^2}{2\sigma^2_{-z}} \right)$$
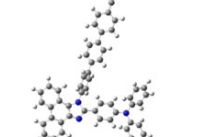
(4)
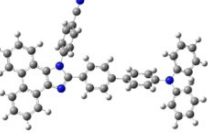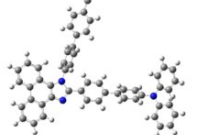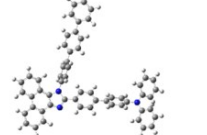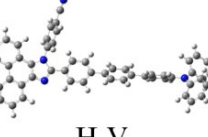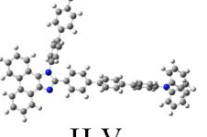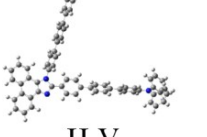
In Equation 4, A_+ and A_- are the normalized factors that ensure the integrated charge on the centroid to be equal to the corresponding density change integrated in the whole space.

SI-3: Optimized geometry and UV wavelengths

We divide 18 molecules into two groups: cyano-free, which named in lowercase; cyano-substituted, which named in uppercase. All the molecules are named according to the number of benzene on the backbone and the branch. For example, h_1v_3 means cyano-free series, horizontal backbone one benzene ring and vertical branch three benzene rings.

LE\CT	1 phenyl	2 phenyl	3 phenyl
1 phenyl	h_1v_1	h_1v_2	h_1v_3
2 phenyl	h_2v_1	h_2v_2	h_2v_3
3 phenyl	h_3v_1	h_3v_2	h_3v_3

(a)

LE\CT	1 phenyl	2 phenyl	3 phenyl
1 phenyl	H_1V_1	H_1V_2	H_1V_3
2 phenyl	H_2V_1	H_2V_2	H_2V_3
3 phenyl	H_3V_1	H_3V_2	H_3V_3

(b)

Figure S2. Optimized geometries of (a) cyano-free molecules and (b) cyano-substituted molecules.

Figure S3. Solvent effect of UV spectra of h_2v_1, H_1V_1 and H_2V_1

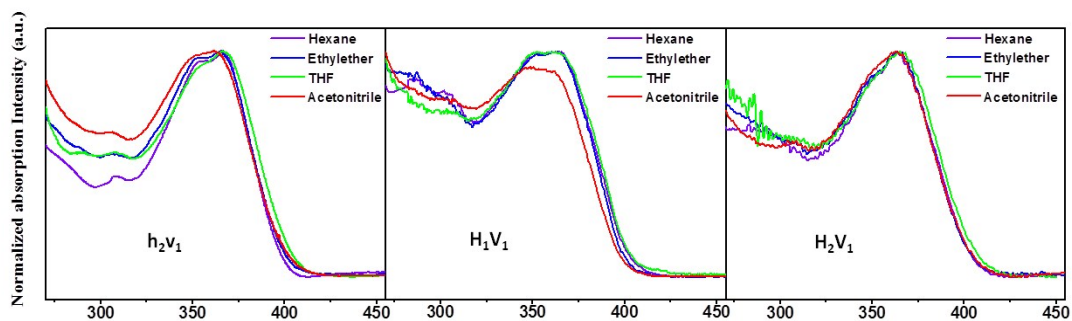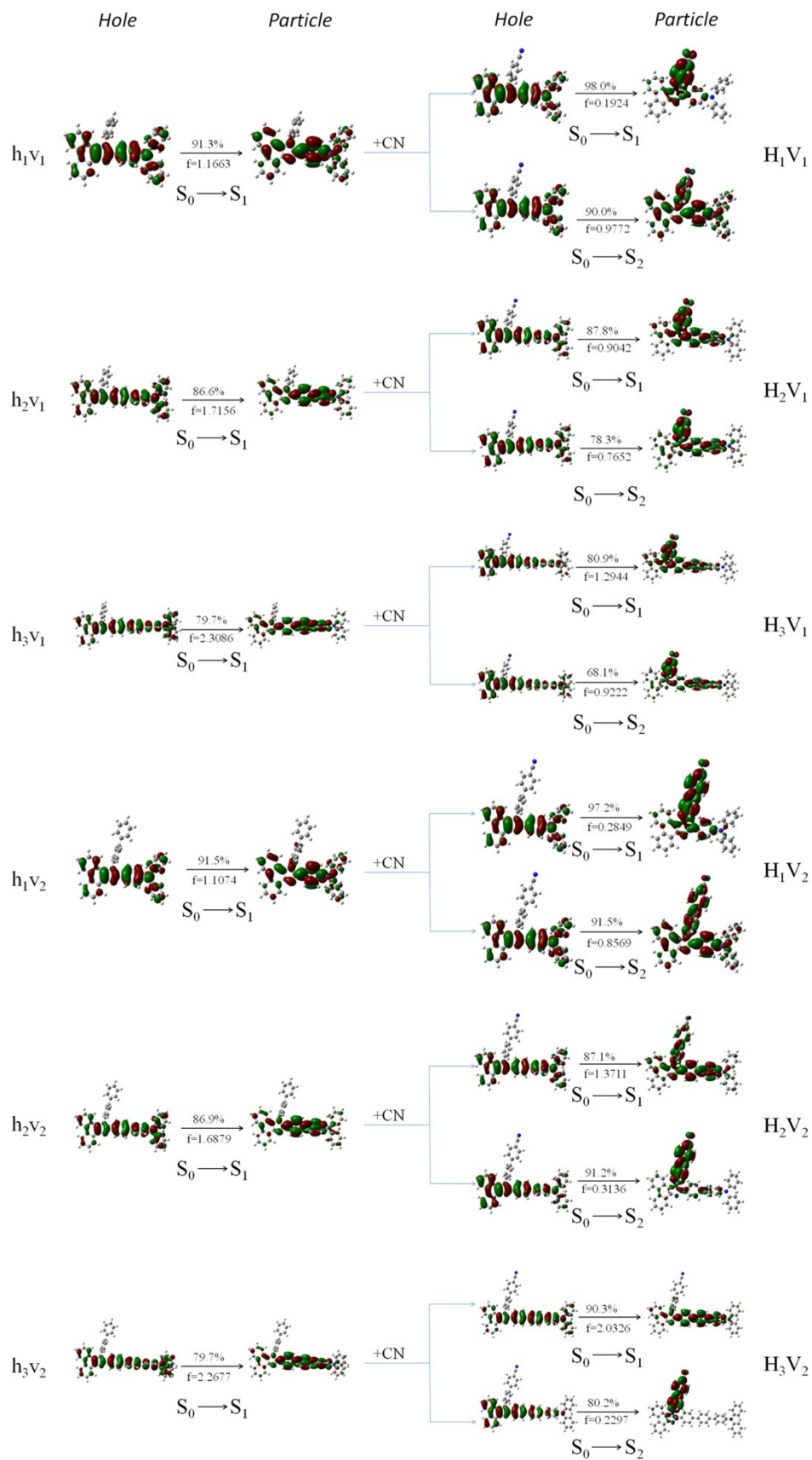**SI-4: NTOs and Centroids of charges of S1 and S2 states of cyano-substituend molecules compared with NTOs of S1 of cyano-free molecules and corresponding calculation data.**
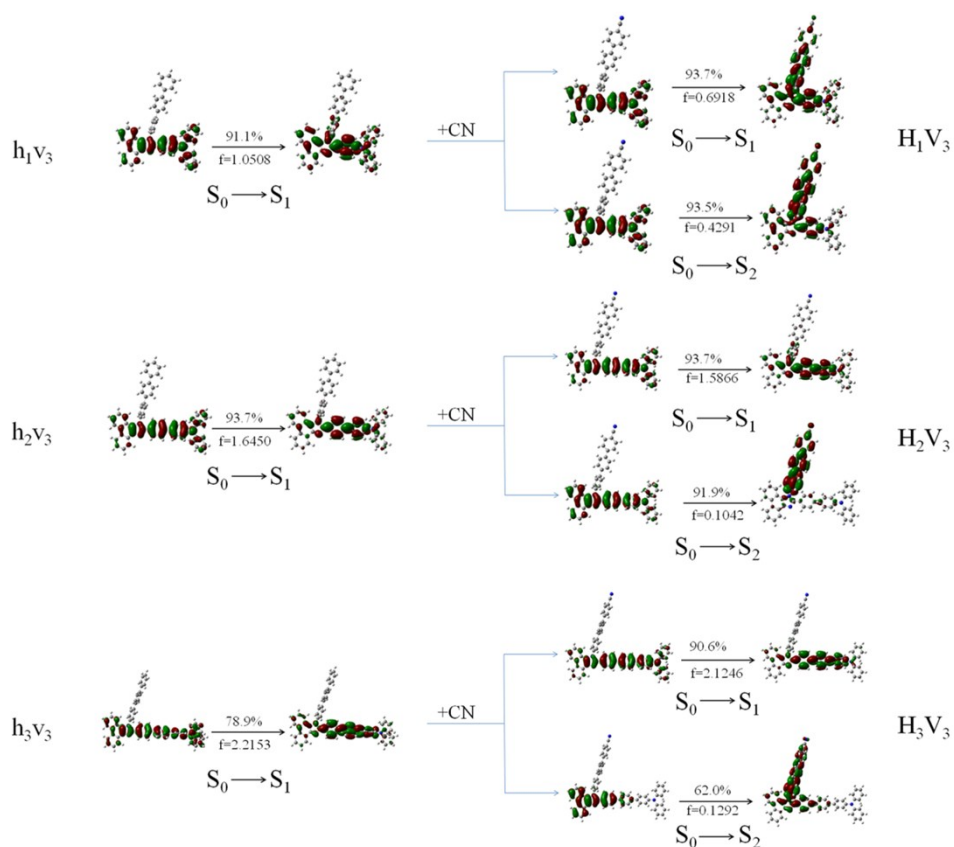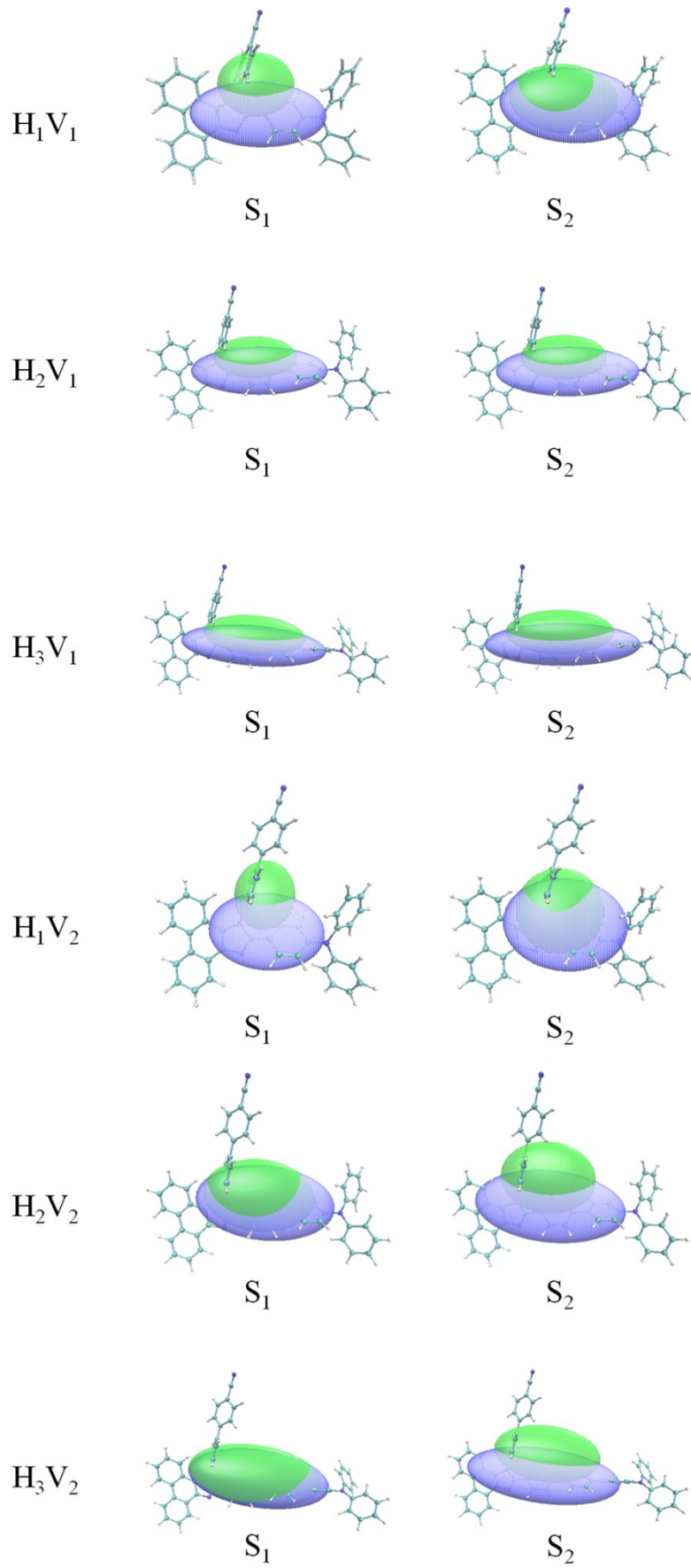
Hole   *Particle*   *Hole*   *Particle*

h_1v_1 $\xrightarrow[f=1.1663]{91.3\%}$ +CN $\xrightarrow[f=0.1924]{98.0\%}$ $S_0 \longrightarrow S_1$ H_1V_1

$S_0 \longrightarrow S_1$ $\xrightarrow[f=0.9772]{90.0\%}$ $S_0 \longrightarrow S_2$

h_2v_1 $\xrightarrow[f=1.7156]{86.6\%}$ +CN $\xrightarrow[f=0.9042]{87.8\%}$ $S_0 \longrightarrow S_1$ H_2V_1

$S_0 \longrightarrow S_1$ $\xrightarrow[f=0.7652]{78.3\%}$ $S_0 \longrightarrow S_2$

h_3v_1 $\xrightarrow[f=2.3086]{79.7\%}$ +CN $\xrightarrow[f=1.2944]{80.9\%}$ $S_0 \longrightarrow S_1$ H_3V_1

$S_0 \longrightarrow S_1$ $\xrightarrow[f=0.9222]{68.1\%}$ $S_0 \longrightarrow S_2$

h_1v_2 $\xrightarrow[f=1.1074]{91.5\%}$ +CN $\xrightarrow[f=0.2849]{97.2\%}$ $S_0 \longrightarrow S_1$ H_1V_2

$S_0 \longrightarrow S_1$ $\xrightarrow[f=0.8569]{91.5\%}$ $S_0 \longrightarrow S_2$

h_2v_2 $\xrightarrow[f=1.6879]{86.9\%}$ +CN $\xrightarrow[f=1.3711]{87.1\%}$ $S_0 \longrightarrow S_1$ H_2V_2

$S_0 \longrightarrow S_1$ $\xrightarrow[f=0.3136]{91.2\%}$ $S_0 \longrightarrow S_2$

h_3v_2 $\xrightarrow[f=2.2677]{79.7\%}$ +CN $\xrightarrow[f=2.0326]{90.3\%}$ $S_0 \longrightarrow S_1$ H_3V_2

$S_0 \longrightarrow S_1$ $\xrightarrow[f=0.2297]{80.2\%}$ $S_0 \longrightarrow S_2$

Figure S4. Main transition processes of NTOs of all the 18 molecules on S0-geometry following with the oscillator strengths f (under the arrows) and the transition probabilities (above the arrows). Only S1 and S2 states are shown for our interest. From NTO analysis we can see that the S1 and S2 states of cyano-substituted molecules have the same wavefunction shapes on main backbone but different phase on the branch except for H_2V_2 and H_3V_3 molecules (phase reversion phonomenon occurs on the main backbone, which we guess is caused by the program calculation), and the sum of oscillator strengths of S1 and S2 states of cyano-substituted molecules almost equal to that of S1 states of corresponding cyano-free molecules.
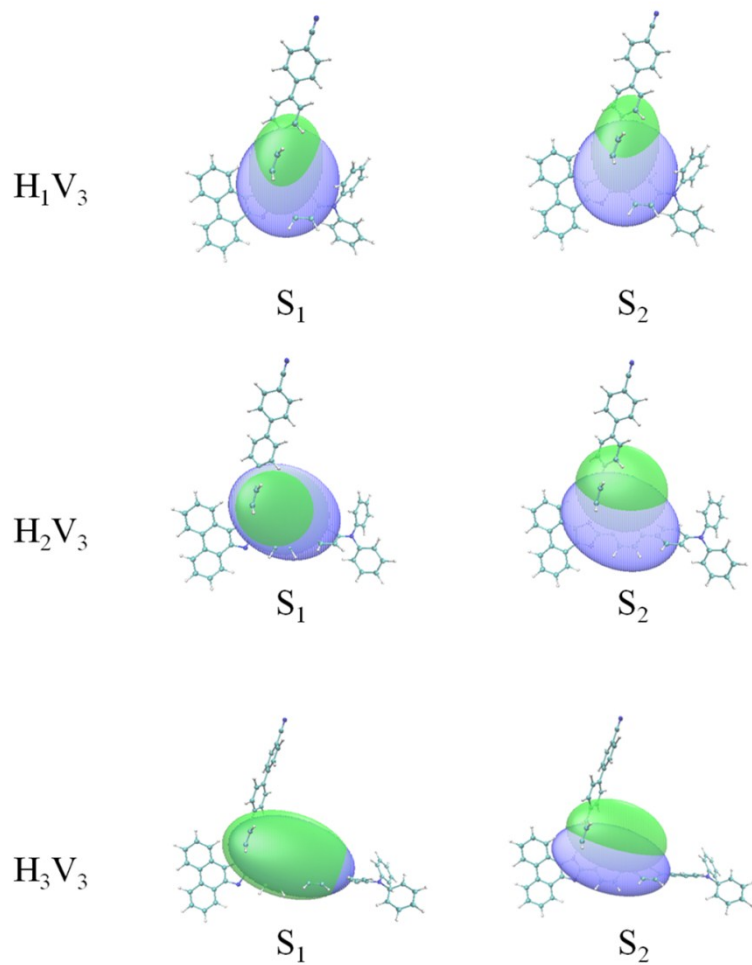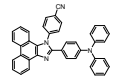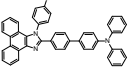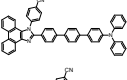
Hole-particle distribution

	S_1	S_2
H_1V_1		
H_2V_1		
H_3V_1		
H_1V_2		
H_2V_2		
H_3V_2		
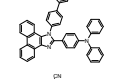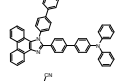
Figure S5. hole-particle distributions of S1 and S2 states of cyano-substituted molecules on S0-geometry. Green areas and blue areas refer to the zones where the electron density is partily increased and decreased respectively.
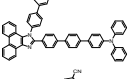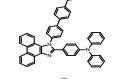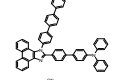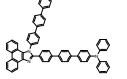
Table S2. Calculated overlap integral and distance of CT of S1 and S2 states of cyano-subsituted molecules on S0-geometry. The smaller overlap integral and larger distance of CT, the more character of CT the state has.

Molecule structure	Lable	Excited state	Overlap integral	Distance of CT(Å)
	H_1V_1	S_1	0.869	2.233
		S_2	0.979	0.808
	H_2V_1	S_1	0.947	1.299
		S_2	0.938	1.379
	H_3V_1	S_1	0.958	1.053
		S_2	0.940	1.279
	H_1V_2	S_1	0.886	2.739
		S_2	0.972	1.145
	H_2V_2	S_1	0.985	0.892
		S_2	0.896	2.642
	H_3V_2	S_1	0.997	0.546
		S_2	0.903	2.486
	H_1V_3	S_1	0.963	1.634
		S_2	0.934	2.593
	H_2V_3	S_1	0.990	0.531
		S_2	0.927	3.209
	H_3V_3	S_1	0.998	0.465
		S_2	0.947	2.677

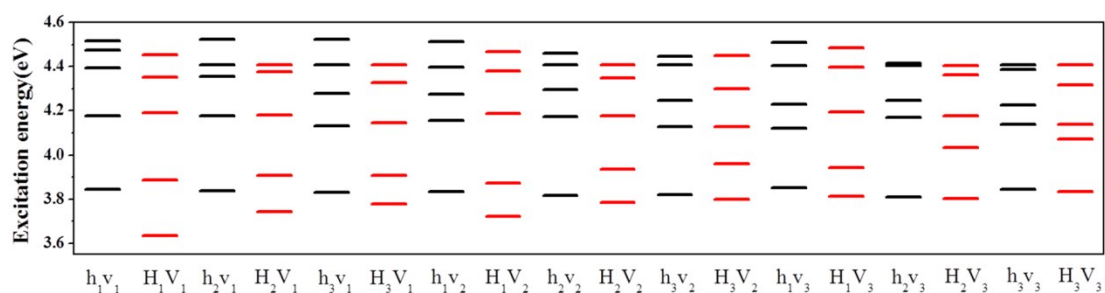**SI-5: The excitation energy diagram of S1-S5 states**

Figure S6. Excitation energies of first five singlet states of all the 18 molecules on S0-geometry. Dark lines and red lines represent the cynao-free and cynao-substituent molecules respectively.

SI-6: Transition density matrix color-filled map of S1 and S2 states of cyano-substituted molecules and corresponding calculation data.
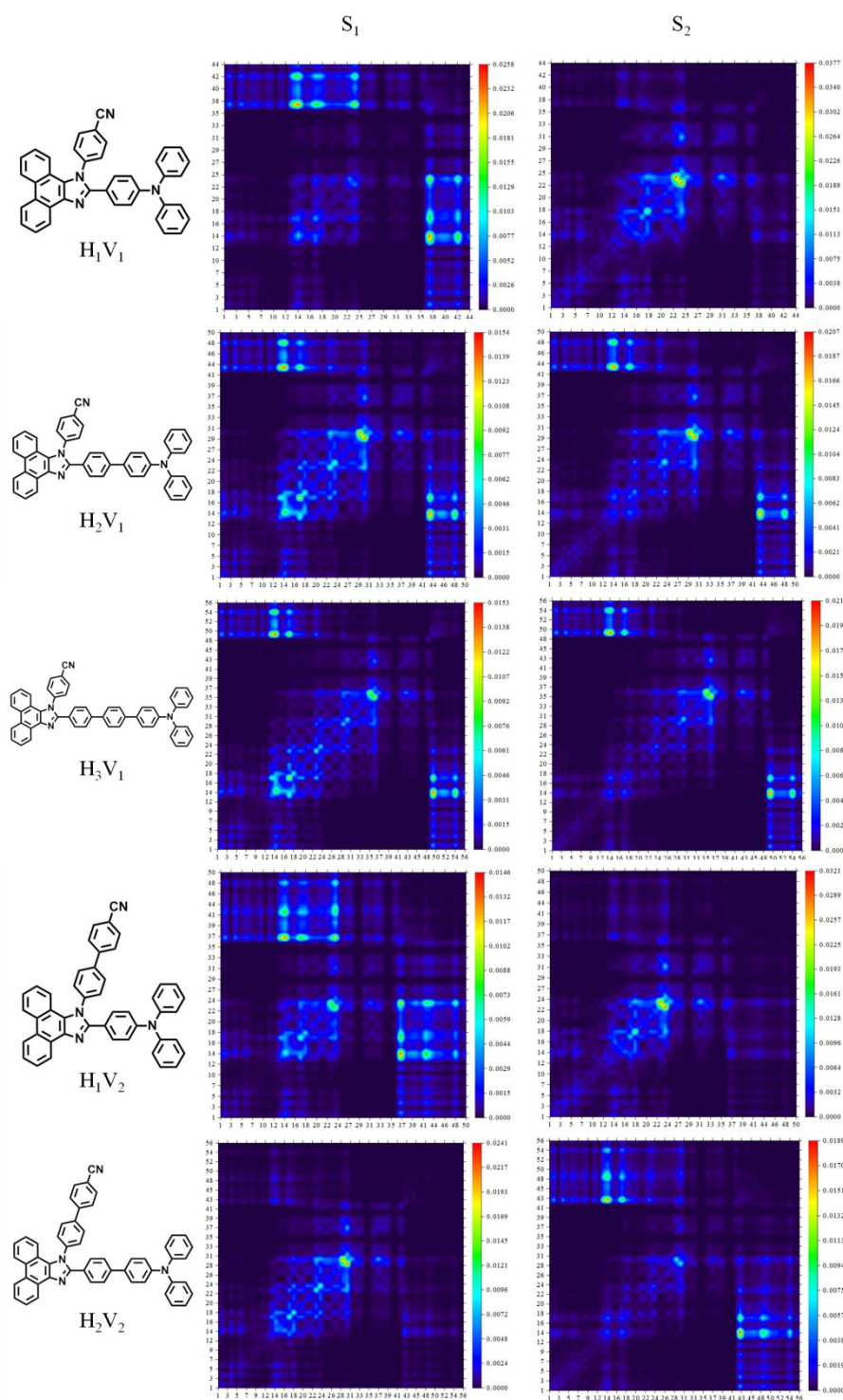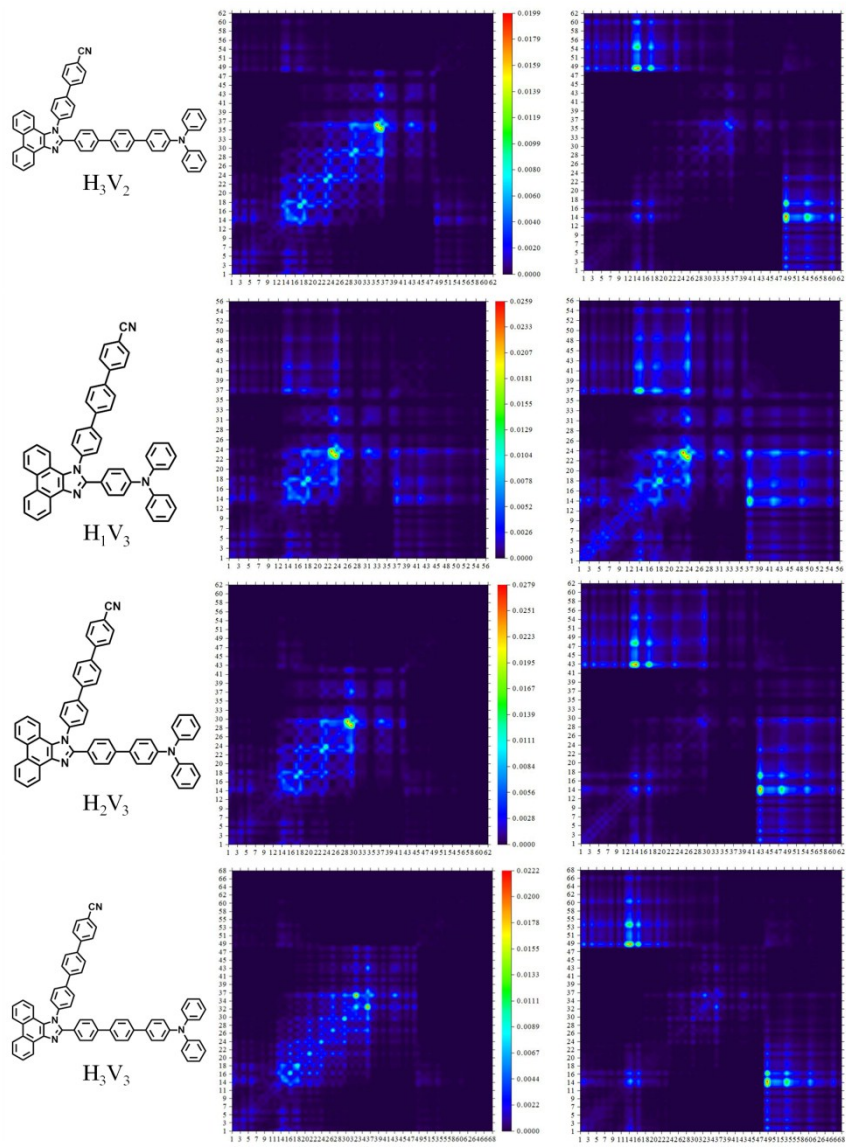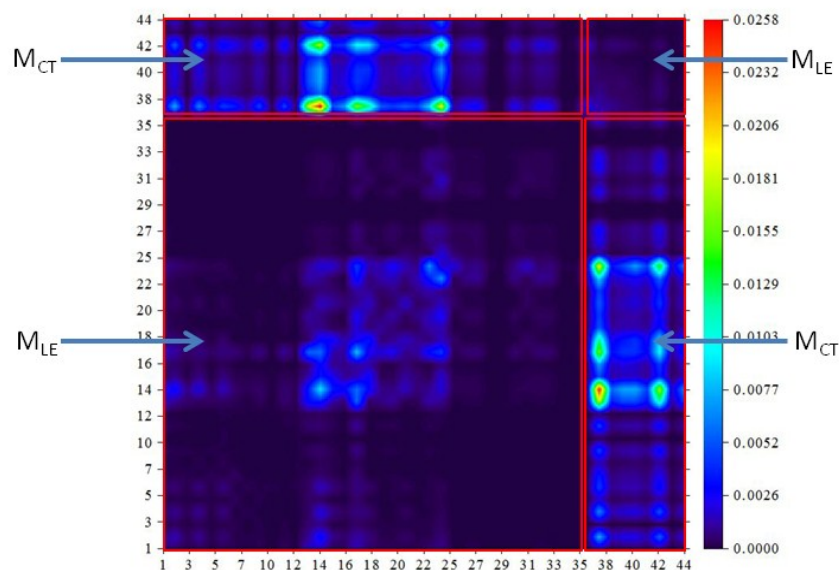
(a)
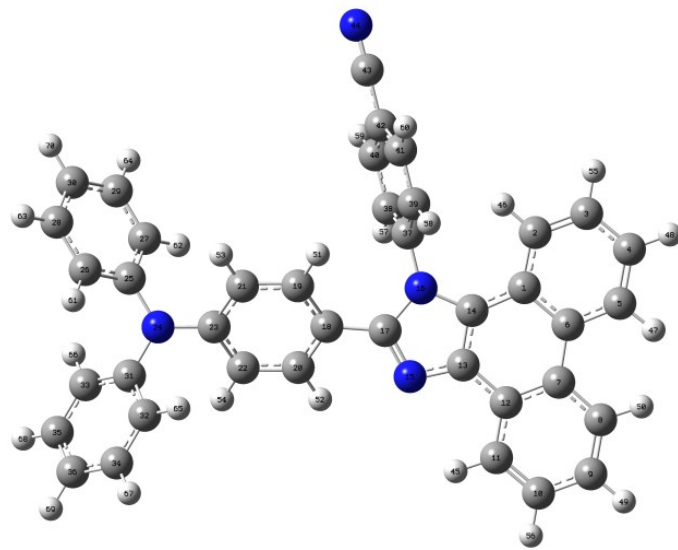
(b)

(c)

Figure S7. transition density matrix color-filled map (a) of S1 and S2 states of cyano-substituted molecules on S0-geometry. Labels in abscissa and ordinate correspond to indices of heavy atoms, for clarity, the correspondence between labels and atoms is marked on the plot (b) by taking H_1V_1 molecules as an example. We order the atoms by labeling the main backbone first and then the branch. Since hydrogen atoms usually have little contribution to the transitions we are interested in, they are usually ignored by default. According to this, we divide the transition density marix color-filled map into LE and CT areas (c), and evaluate the contents of them by using the equations below:

$$R_{LE} = \frac{M_{LE}}{M_{LE} + M_{CT}}$$

$$R_{CT} = \frac{M_{CT}}{M_{LE} + M_{CT}}$$

In equations, R_{LE}, R_{CT} represent the ratios of LE and CT in states, M_{LE}, M_{CT} represent the sum of the matrix elements in LE and CT areas respectively.

Table S3. Contents of LE and CT of S_1 and S_2 states of cyano-substituted molecules on S0-geometry by using the equations above.

	H_1V_1		H_2V_1		H_3V_1		H_1V_2		H_2V_2		H_3V_2		H_1V_3		H_2V_3		H_3V_3	
	S_1	S_2	S_1	S_2	S_1	S_2	S_1	S_2	S_1	S_2	S_1	S_2	S_1	S_2	S_1	S_2	S_1	S_2
LE%	28.7	86.7	61.8	58.5	64.8	57.0	33.8	78.8	84.0	30.8	91.0	26.4	66.6	47.4	94.9	18.8	95.9	26.9
CT%	71.3	13.3	38.2	41.5	35.2	43.0	66.2	21.2	16.0	69.2	9.0	73.6	33.4	52.6	5.1	81.2	4.1	73.1

[SI-1]   Le Bahers T, Adamo C, Ciofini I. *Journal of Chemical Theory and Computation*, **2011**, 7(8): 2498-2506.