Electronic Supplementary Material (ESI) for Materials Horizons.

Supplementary Information:

# Relating Reorganization Energies, Exciton Diffusion Length and Non-Radiative Recombination to the Room Temperature UV-Vis Absorption Spectra of NF-SMA

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## SI 1. Method

**Experimental details:** Y6 and N3 was purchased from eFlexPV Limited, all other NF-SMAs were purchased from 1-Material Incorporation. Following is the full chemical name of materials.

**ITIC:** (2,2′-[[6,6,12,12-Tetrakis(4-hexylphenyl)-6,12-dihydrodithieno[2,3-d:2′,3′-d′]-s-indaceno[1,2-b:5,6-b′]dithiophene-2,8-diyl]bis [methylidyne (3-oxo-1H-indene-2,1(3H) diylidene)]] bis[propanedinitrile])

**ITIC-4F:** (3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2′,3′-d′]-s-indaceno[1,2-b:5,6-b′]dithiophene)

**ITM:** (3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6/7-methyl)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2′,3′-d′]-s-indaceno[1,2-b:5,6-b′]dithiophene)

**Y6:** (2,2′-((2Z,2′Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e] hieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2′,3′:4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene)) bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile),

**N3:** (2,2′-((2Z,2′Z)-((12,13-bis(3-ethylheptyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e] thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2′,3′:4,5]thieno[3,2-b]indole-2,10-diyl) bis (methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile)

**BTP-eC9:** (2,2′- [[12,13-Bis(2-butyloctyl)-12,13-dihydro-3,9-dinonylbisthieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-e:2′,3′-g][2,1,3]benzothiadiazole-2,10-diyl]bis [methylidyne (5,6-chloro-3-oxo-1H-indene-2,1(3H)-diylidene) ]]bis[propanedinitrile

**IEICO-4F:** (2,2′-((2Z,2′Z)-(((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-sindaceno[1,2-b:5,6-b′]dithiophene-2,7-diyl)bis(4-((2-ethylhexyl)oxy)thiophene-5,2-diyl))bis (methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile),

**IEICO-4Cl:** (2,2′-((2Z,2vZ)-(((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-sindaceno[1,2-b:5,6-b′]dithiophene-2,7-diyl)bis(4-((2-ethylhexyl)oxy)thiophene-5,2-ziyl))bis(methanylylidene)) bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile),

**O-IDTBR:** ((5Z,5′Z)-5,5′-((7,7′-(4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b′]dithiophene-2,7-diyl)bis(benzo[c][1,2,5]thiadiazole-7,4-diyl))bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one))

**EH-IDTRB:** (5,5′-[[4,4,9,9-tetrakis(2-ethylhexyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b′]dithiophene-2,7-diyl]bis(2,1,3-benzothiadiazole-7,4-diylmethylidyne)]bis[3-ethyl-2-thioxo-4-thiazolidinone]).

Solutions of different NF-SMA were prepared in chloroform (CF) at 0.02mg/ml concentration. At such low concentrations, the spectra are attributed to intrachain excitations (single molecule regime). The UV-vis absorption spectra of different samples were recorded using a Cary 50 spectrophotometer. Absorption spectra of solution with 0.1mg/ml concentrations was measured using a 1mm quartz cuvette to avoid saturation of signal. For 0.02 mg/ml concentrations a regular quartz 1cm cuvette was used. The photoluminescence (PL) spectra were carried out with a Fluorometer FLS 980 in the IMEKS laboratory at NCSU. A regular 1 cm quartz cuvette was used to measure PL spectra for both concentrations.

**Quantum mechanical (QM) calculations:** All calculations were performed with the Gaussian 09 package employing the DFT or TD-DFT methodologies[1] computing resources provided by North Carolina State University High Performance Computing Services Core Facility (RRID:SCR 022168). The geometry of NF-SMAs were optimized for different functionals: B3LYP, PBE0 and wB97XD, all with a 6-31G(d,p) basis set. Vertical Absorption calculation was done by TD-DFT energy calculation on the ground state geometry for different functional. The Vertical Emission calculation was done by TD-DFT optimization of first excited state geometry following with a TD-DFT energy calculation. The solvent effects were taken into account using the Polarizable Continuum Model (PCM) model for CF when calculating the optical absorption. The side chains are replaced by methyl groups to reduce the computational time unless stated otherwise.

## SI 2. Calculated Population Distribution at Different Dihedral Angles

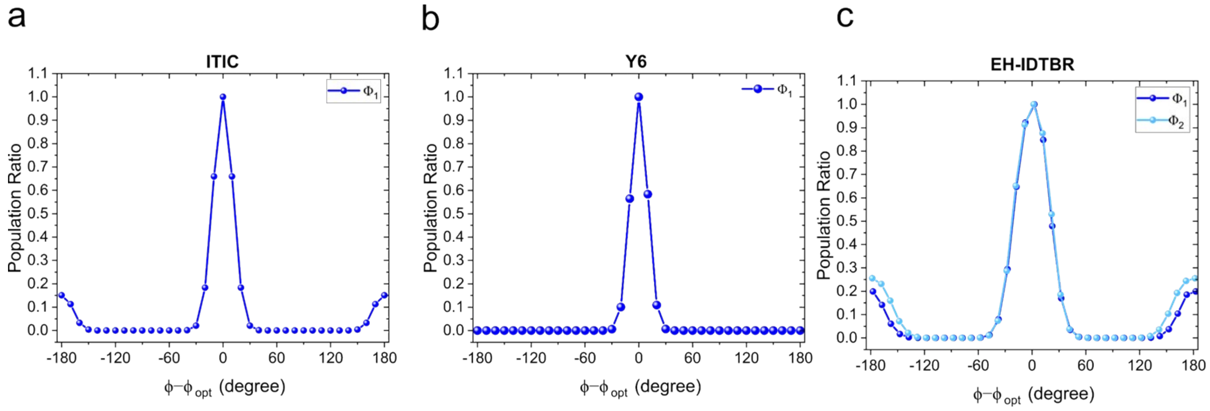

**Figure S1** Calculated population distribution using Boltzmann distribution at room temperature at different dihedral angles for a) ITIC, b) Y6 and c) EH-IDTBR.

## SI 3. DFT/TD-DFT Calculation of Excited States

### B3LYP functional

**Table S1** DFT/TD-DFT results of the first three singlet excited states calculated using B3LYP functional with 6-31G(d,p) basis set considering CF as the solvent.

| Molecule | Transition | $\varepsilon_{S_0 \to S_i}$ (eV) | Magnitude TDM (Deby) | TDM vector (Deby) | OSC. S |
|---|---|---|---|---|---|
| **ITIC** | $S_0 \to S_1$ | 1.773 | 8.359 | (8.357, -0.214, 0.000) | 3.036 |
|  | $S_0 \to S_2$ | 2.120 | 0.000 | (0.000, 0.000, 0.000) | 0.000 |
|  | $S_0 \to S_3$ | 2.455 | 1.966 | (1.898, 0.514, 0.000) | 0.216 |
| **Y6** | $S_0 \to S_1$ | 1.713 | 7.554 | (7.554, 0.000, -0.008) | 2.395 |
|  | $S_0 \to S_2$ | 2.052 | 1.839 | (-0.000, 1.839, 0.000) | 0.170 |
|  | $S_0 \to S_3$ | 2.329 | 1.443 | (1.443, 0.000, -0.011) | 0.119 |
| **EH-IDTBR** | $S_0 \to S_1$ | 1.579 | 8.106 | (-8.105, -0.119, 0.000) | 2.542 |
|  | $S_0 \to S_2$ | 1.868 | 0.058 | (0.000, 0.000, 0.058) | 0.000 |
|  | $S_0 \to S_3$ | 2.752 | 0.092 | (0.000, 0.000, -0.093) | 0.0005 |

### wB97XD functional

**Table S2** DFT/TD-DFT results of the first three singlet excited states calculated using wB97XD functional with 6-31G(d,p) basis set

| Molecule | Transition | $\varepsilon_{S_0 \to S_i}$ (eV) | Magnitude TDM (Deby) | TDM vector (Deby) | OSC. S |
|---|---|---|---|---|---|
| **ITIC** | $S_0 \to S_1$ | 1.808 | 8.363 | (-8.360,0.225,0.000) | 3.098 |
|  | $S_0 \to S_2$ | 2.172 | 0.000 | (0.000, 0.000, 0.000) | 0.000 |
|  | $S_0 \to S_3$ | 2.534 | 1.930 | (-1.854, -0.539, 0.000) | 0.231 |
| **Y6** | $S_0 \to S_1$ | 1.176 | 7.309 | (-7.303, 0.000, 0.275) | 2.309 |
|  | $S_0 \to S_2$ | 2.108 | 2.131 | (0.000, -2.131, 0.000) | 0.2345 |
|  | $S_0 \to S_3$ |  |  |  |  |
| **EH-IDTBR** | $S_0 \to S_1$ | 1.674 | 7.671 | (7.669, 0.150, -0.006) | 2.413 |
|  | $S_0 \to S_2$ | 1.947 | 0.014 | (-0.014, 0.000, 0.004) | 0.002 |
|  | $S_0 \to S_3$ | 2.417 | 0.191 | (-0.145, -0.027, -0.121) | 0.002 |

considering CF as the solvent.

## PBE0 functional

**Table S3** DFT/TD-DFT results of the first three singlet excited states calculated using B3LYP functional with 6-31G(d,p) basis set considering CF as the solvent.

| Molecule | Transition | $\varepsilon_{S_0 \to S_i}$ (eV) | Magnitude TDM (Deby) | TDM vector (Deby) | OSC. S |
|---|---|---|---|---|---|
| **ITIC** | $S_0 \to S_1$ | 1.403 | 8.064 | (8.058, -0.327, 0.000) | 2.236 |
| | $S_0 \to S_2$ | 1.517 | 0.000 | (0.000, 0.000, 0.000) | 0.000 |
| | $S_0 \to S_3$ | 1.796 | 3.593 | (3.581, 0.292, 0.000) | 0.568 |
| **Y6** | $S_0 \to S_1$ | 1.374 | 7.093 | (-7.093, 0.000, -0.001) | 1.694 |
| | $S_0 \to S_2$ | 1.484 | 0.888 | (0.000, -0.888, 0.000) | 0.029 |
| | $S_0 \to S_3$ | 1.703 | 0.350 | (0.000, -0.350, 0.000) | 0.005 |
| **EH-IDTBR** | $S_0 \to S_1$ | 1.198 | 8.570 | (-8.570, 0.011, 0.000) | 2.155 |
| | $S_0 \to S_2$ | 1.301 | 0.014 | (-0.000, 0.000, -0.015) | 0.000 |
| | $S_0 \to S_3$ | 1.774 | 0.010 | (0.000, 0.000, 0.010) | 0.000 |

## Geometry optimized using B3LYP function and energy calculation is done using PBE0 functional

**Table S4** DFT/TD-DFT results of the first three singlet excited states calculated using wB97XD functional with 6-31G(d,p) basis set

| Molecule | Transition | $\varepsilon_{S_0 \to S_i}$ (eV) | Magnitude TDM (Deby) | TDM vector (Deby) | OSC. S |
|---|---|---|---|---|---|
| **ITIC** | $S_0 \to S_1$ | 1.446 | 7.811 | (7.806, -0.295, 0.000) | 2.162 |
| | $S_0 \to S_2$ | 1.567 | 0.000 | (0.000, 0.000, 0.000) | 0.000 |
| | $S_0 \to S_3$ | 1.861 | 0.867 | (-0.746, -0.005, 0.000) | 0.5012 |
| **Y6** | $S_0 \to S_1$ | 1.413 | 7.000 | (7.006, 0.000, -0.003) | 1.700 |
| | $S_0 \to S_2$ | 1.534 | 0.973 | (-0.001, 0.973, 0.000) | 0.036 |
| | $S_0 \to S_3$ | 1.731 | 0.344 | (0.000, -0.344, 0.000) | 0.005 |
| **EH-IDTBR** | $S_0 \to S_1$ | 1.247 | 8.141 | (-8.141, -0.007, 0.000) | 2.024 |
| | $S_0 \to S_2$ | 1.360 | 0.020 | (0.000, 0.000, -0.019) | 0.000 |
| | $S_0 \to S_3$ | 1.834 | 0.010 | (-0.006, 0.003, 0.010) | 0.000 |

considering CF as the solvent.

**Table S5** Comparison between experimental values of excitation energies derived from FC analyses and TD-DFT results for ITIC, Y6 and EH-IDTBR molecules in CF calculated using three different functionals.

*SE is the difference between calculated and experimentally measured (FC analysis) of excitation energies.

| **Molecule** | **Experiment (FC analysis)** | **Calculations** | | | | | |
|---|---|---|---|---|---|---|---|
| | | **B3LYP** | | **wB97XD** | | **PBE0** | |
| | **Energy(eV)** | **Energy(eV)** | **SE (eV)*** | **Energy(eV)** | **SE (eV)*** | **Energy(eV)** | **SE (eV)*** |
| **ITIC** | 1.82 ($s_0 \rightarrow s_1$) | 1.77 ($s_0 \rightarrow s_1$) | 0.05 | 1.81 ($s_0 \rightarrow s_1$) | 0.01 | 1.40 ($s_0 \rightarrow s_1$) | 0.42 |
| **Y6** | 1.69 ($s_0 \rightarrow s_1$) | 1.71 ($s_0 \rightarrow s_1$) | -0.02 | 1.76 ($s_0 \rightarrow s_1$) | -0.07 | 1.37($s_0 \rightarrow s_1$) | 0.32 |
| | 2.08 ($s_0 \rightarrow s_2$) | 2.05 ($s_0 \rightarrow s_2$) | 0.03 | 2.11 ($s_0 \rightarrow s_2$) | -0.03 | 1.48 ($s_0 \rightarrow s_2$) | 0.60 |
| **EH-IDTBR** | 1.89 ($s_0 \rightarrow s_1$) | 1.58 ($s_0 \rightarrow s_1$) | 0.31 | 1.67 ($s_0 \rightarrow s_1$) | 0.22 | 1.20 ($s_0 \rightarrow s_1$) | 0.69 |

## SI 4. Classical Franck-Condon Model

The absorption spectra are usually recorded and presented in wavelength scale. In order to properly analyze the spectra, it should be corrected for both wavelength to energy conversion and Photon Density of States (DOS).

Required Spectra correction before FC analysis:

1. Jacobian conversion of spectral data from wavelength to energy representation is an important step that is commonly neglected in literature[2].

$$I(\varepsilon) = I(\lambda)\frac{d\lambda}{d\varepsilon} = I(\lambda)\frac{1240}{\varepsilon^2} \qquad \text{(Eq.S-1)}$$

2. Since the density of photons in the medium surrounding the emitter or absorber is not constant at different energies, the recorded spectra need to be corrected for the photon DOS before FC or any population analysis. This effect implies that the photoluminescence and absorption spectra should be normalize by factor of $[n(\varepsilon).\varepsilon]^3$ and $[n(\varepsilon).\varepsilon]$ respectively, where $n(\varepsilon)$ is the refractive index of the surrounding medium at transition energy $\varepsilon$[3].

Considering the above-mentioned correction for the normalized absorption spectra, the FC model for a single molecule with one contributing electronic transition ($S_0 \rightarrow S_1$), and one effective vibrational mode can be expressed as follows:

$$Normalized\left(\frac{I_{abs}(\varepsilon)}{n(\varepsilon)\varepsilon}\right) = exp(-s)\sum_{m=0} \frac{s^m}{m!}\exp\left[-\frac{\left(\varepsilon - \left(\varepsilon_{S_0 \rightarrow S_1} + m\hbar\omega_{vib}\right)\right)^2}{2\sigma^2}\right] \qquad \text{(Eq.S-2)}$$

where $S_j$ denotes j^th^ electronic state, and $\varepsilon_{S_0 \rightarrow S_j}$ is the energy $S_0 \rightarrow S_j$ electronic transition. m=0, 1, 2… denotes number of contributing overtones for the effective vibrational mode with energy $\hbar\omega_{vib}$. s is total Huang Rhys factor for the jth electronic transition. A gaussian line shape with constant standard deviation ($\sigma$) is assumed for all overtones. The simple FC model in equation S-2 can be expanded as the number of contributions to the absorption spectra increase. This includes multiple vibrational mode, multiple electronic transition, or coexistence of different species in the system.

## SI 5. FC Analysis of ITIC Absorption Spectra in Solution

Equation S-3 is the model used for fitting ITIC absorption spectra in solution:

$$Normalized\left(\frac{I_{abs}(\varepsilon)}{n(\varepsilon)\varepsilon}\right) = a.exp(-s)\sum_{m=0}^{3}\frac{s^m}{m!}\exp\left[-\frac{\left(\varepsilon-\left(\varepsilon_{S_0\to S_1}+m\hbar\omega_{vib}\right)\right)^2}{2\sigma^2}\right] \quad \text{(Eq. S-3)}$$

$\varepsilon_{S_0\to S_1}$ is 0-0 transition energy for the first electronic excited state, $\varepsilon_{vib}$ is the vibrational energy for the effective mode. We assumed a Gaussian line shape function with similar standard deviation $\sigma$ for all the vibrational overtones. **s** is the Huang-Rhys (HR) parameter and equal to $0.38$. The expression is multiplied by a constant "a" since the corrected absorption spectrum is normalized to 1. **Table S- 6** contains all the fitting parameter used for FC modeling of ITIC.

**Table S6** The parameters used in the fitting of absorption spectrum of ITIC in CF solution.

| $s$ | $\varepsilon_{S_0\to S_1}(eV)$ | $\sigma(eV)$ | $FWHM(eV)$ | $\hbar\omega_{vib}$(eV) |
|---|---|---|---|---|
| 0.380 | 1.818 | 0.064 | 0.150 | 0.169 |

## SI 6. FC Analysis of Y6 Absorption Spectra in Solution

Equation S-4 is the mathematical expression used for the fitting the absorption spectra of Y6 in solution.

$$Normalized\left(\frac{I_{abs}(\varepsilon)}{n(\varepsilon)\varepsilon}\right) = \sum_{j=1}^{2} a_{S_0\to S_j} e^{-(s_j)} \left\{ \exp\left[-\frac{\left(\varepsilon - \varepsilon_{S_0\to S_j}\right)^2}{2\sigma}\right] + \sum_{i=1}^{2}\sum_{m=1}^{2} \frac{(s_{j,i})^m}{m!} \exp\left[-\frac{\left(\varepsilon - \left(\varepsilon_{S_0\to S_j} + m\hbar\omega_{vib}\right)\right)^2}{2\sigma_i^2}\right]\right\} \quad \text{(Eq.S-4)}$$

In above equation the summation over j accounts for two electronic transition contributions, and the summation over i takes the two different vibrational modes into account. $\varepsilon_{S_0\to S_j}$ is the energy of 0-0 transition of the jth electronic transition. $S_{j,i}$ denotes HR parameter of ith contributing vibrational mode in the jth electronic state and $s_j = \sum_i s_{j,i}$ is the total HR parameter for jth electronic transition. $\hbar\omega_{vib}$ is the energy of vibrational mode "i", $\sigma_i$ is standard deviation of the Gaussian line shape, which is assumed to be different for each of vibrational modes. $A_{S_0\to S_j}$ is a constant that accounts for the contribution of $S_0\to S_j$ electronic transition into the spectrum. **Table S-7** contains the fitting parameters of Y6. It should be noted that we only consider the region between 1.4-2.4eV for the fitting purposes.

**Table S7** The parameters used in the fitting of absorption spectrum of Y6 in CF solution.
*σ=standard deviation for 0-0 transitions.

| Fitting parameter | Vibration mode (i) or electronic transition (j) | Value |
|---|---|---|
| $\hbar\omega_{vib,i}(eV)$ | $i=1$ | 0.154 |
| | $i=2$ | 0.180 |
| $\sigma_i(eV)$ | $i=1$ | 0.0677 (FWHM=0.159) |
| | $i=2$ | 0.0870 (FWHM=0.205) |
| $\sigma(eV)*$ | | 0.0560 (FWHM=0.132) |
| $a_{S_0\to S_j}$ | $j=1$ | 1.313 |
| | $j=2$ | 0.155 |
| $\varepsilon_{S_0\to S_j}(eV)$ | $j=1$ | 1.686 |
| | $j=2$ | 2.085 |
| $s_j = s_{j,i=1} + s_{j,i=2}$ | $j=1$ | 0.311=0.175+0.136 |
| | $j=2$ | 0.376=0.317+0.059 |

## SI 7. FC Analysis of EH-IDTBR Absorption Spectra in Solution

Equation S-5 is the mathematical expression used for the fitting the absorption spectra of EH-IDTBR in CF solution. In this model we assumed two populations and one vibrational mode.

$$Normalized\left(\frac{I_{abs}(\varepsilon)}{n(\varepsilon)\varepsilon}\right) = \sum_{j=1}^{2} a_j e^{-(s_j)} \left\{ \exp\left[-\frac{\left(\varepsilon - \varepsilon_{S_0 \to S_1}\right)^2}{2\sigma}\right] + \sum_{m=1}^{2} \frac{(s_j)^m}{m!} \exp\left[-\frac{\left(\varepsilon - \left(\varepsilon_{S_0 \to S_1} + m\hbar\omega_{vib}\right)\right)^2}{2\sigma_j^2}\right]\right\} \qquad \text{(Eq.S-5)}$$

In above equation the summation over j accounts for two different populations. $\varepsilon_{S_0 \to S_j}$ is the energy of 0-0 transition for the first electronic transition in the j^th^ population. $s_j$ denotes HR parameter of j^th^ contributing population. $\hbar\omega_{vib}$ is the energy of vibrational mode and $\sigma_j$ is standard deviation of the Gaussian line shape, which is assumed to be different for different contributing populations. $a_j$ accounts for the contribution of different populations into the spectra. The fitting parameters are listed **Table S- 8.**

**Table S8** The parameters used in the fitting of absorption spectrum of EH-IDTBR in CF solution using model 2: Two populations with one similar vibrational mode.

| Fitting parameter | Population (j) | Value |
|---|---|---|
| $\hbar\omega_{vib}(eV)$ | | 0.154 |
| $\sigma_j(eV)$ | $j = 1$ | 0.0757 (FWHM=0.184) |
| | $j = 2$ | 0.1612 (FWHM=0.379) |
| $a_{S_0 \to S_j}$ | $j = 1$ | 1.448 |
| | $j = 2$ | 0.1749 |
| $\varepsilon_{S_0 \to S_j}(eV)$ | $j = 1$ | 1.868 |
| | $j = 2$ | 2.034 |
| $s_j$ | $j = 1$ | 0.500 |
| | $j = 2$ | 0.818 |

Due to the broadening effects, one can find multiple FC model that can nicely describe the absorption spectra of EH-IDTBT. For instance, considering only one population, but two different vibrational modes can also yield to a fitting that is in agreement with the experimental data (Figure S 3). Equation S-6 is the mathematical expression of this model:

$$Normalized\left(\frac{I_{abs}(\varepsilon)}{n(\varepsilon)\varepsilon}\right) = a.e^{-(s)} \left\{ \exp\left[-\frac{\left(\varepsilon - \varepsilon_{S_0 \to S_1}\right)^2}{2\sigma}\right] + \sum_{i=1}^{2} \sum_{m=1}^{2} \frac{(s_i)^m}{m!} \exp\left[-\frac{\left(\varepsilon - \left(\varepsilon_{S_0 \to S_1} + m\hbar\omega_{vib}\right)\right)^2}{2\sigma_i^2}\right]\right\} \qquad \text{(eq.S-6)}$$

where the sum over i accounts for two different vibrational modes. $S_i$ denotes HR factor of ith contributing vibrational mode and $S = \sum_{i=1}^{2} S_i$ denotes total HR factor. The fitting parameters of this model are listed in **Table S- 9**. The vibrational energies derived from this model are 135meV (1088 $cm^{-1}$) and 220meV (1774 $cm^{-1}$). These values are not in agreement with the simulated Raman spectra (Figure 4-j), makes this model to be unacceptable.

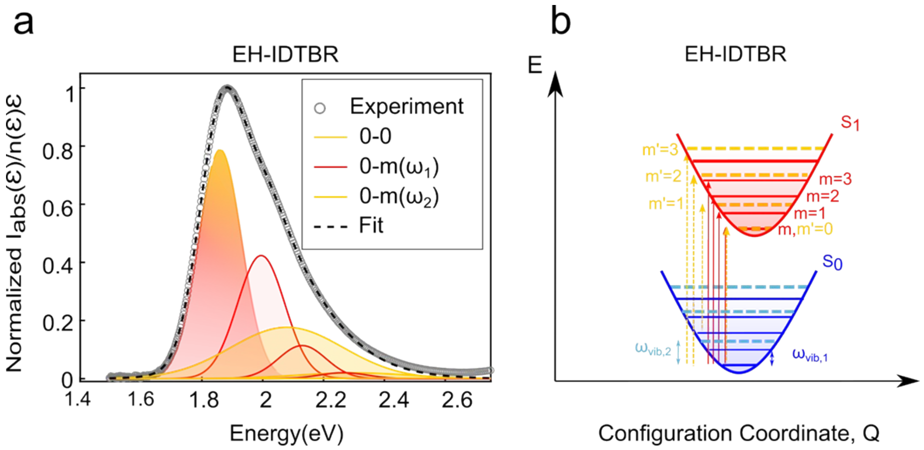

**Figure S2** (a) Normalized absorption spectra of EH-IDTBR in CF solution after both Jacobian and photon DOS corrections (gray open circles). The dashed black line is the FC model of single population-two vibrational mode fitted to the experimental data. (b) Schematic illustration of the FC model. This model gives vibrational energies that are not consistent with the Raman spectra of the molecule.

**Table S9** The parameters used in the fitting of absorption spectrum of EH-IDTBR in CF solution using a model with single population, two vibrational modes with different broadening.

| **Fitting parameter** | **Vibration mode (i)** | **Value** |
|---|---|---|
| $\hbar\omega_{vib}(eV)$ | $i = 1$<br>$i = 2$ | 0.135<br>0.220 |
| $\sigma_i(eV)$ | $i = 1$<br>$i = 2$ | 0.078 (FWHM=0.184)<br>0.185(FWHM=0.435) |
| $\sigma(eV)*$ | | 0.0711 (FWHM=0.167) |
| $a$ | | 1.688 |
| $\varepsilon_{S_0\to S_1}(eV)$ | | 1.86 |
| $s_i$ | $i = 1$<br>$i = 2$ | 0.537<br>0.224 |

### SI 8. Why Y6-like molecules have one conformation population?

As we show in **Figure S3-a** and also discussed by J. Wu et. al., removing the alkyl side chains from the outer core of the backbone results in smaller PES barriers indicating the steric hindrance effect of the sidechains has a significant contribution into the Y6 high conformational uniformity[4]. Moreover, the delocalization of the π-electrons across the system leads to steeper barrier that also acts to lock the conformation[5]; hence, we evaluated the bond length of the bridging C-C atoms among the D and A groups at different dihedral angles for ITIC, Y6 and EH-IDTBR (**Figure S3-c**). Our results show that the bridge in Y6 has the highest double-bond characteristic, as expected. On the other hand, bond lengths for both bridges in EH-IDTBR have smallest double bond characteristics (even in the optimized geometry). So, the nature of π-electrons delocalization in Y6 results in steeper PES barrier and higher conformational uniformity.

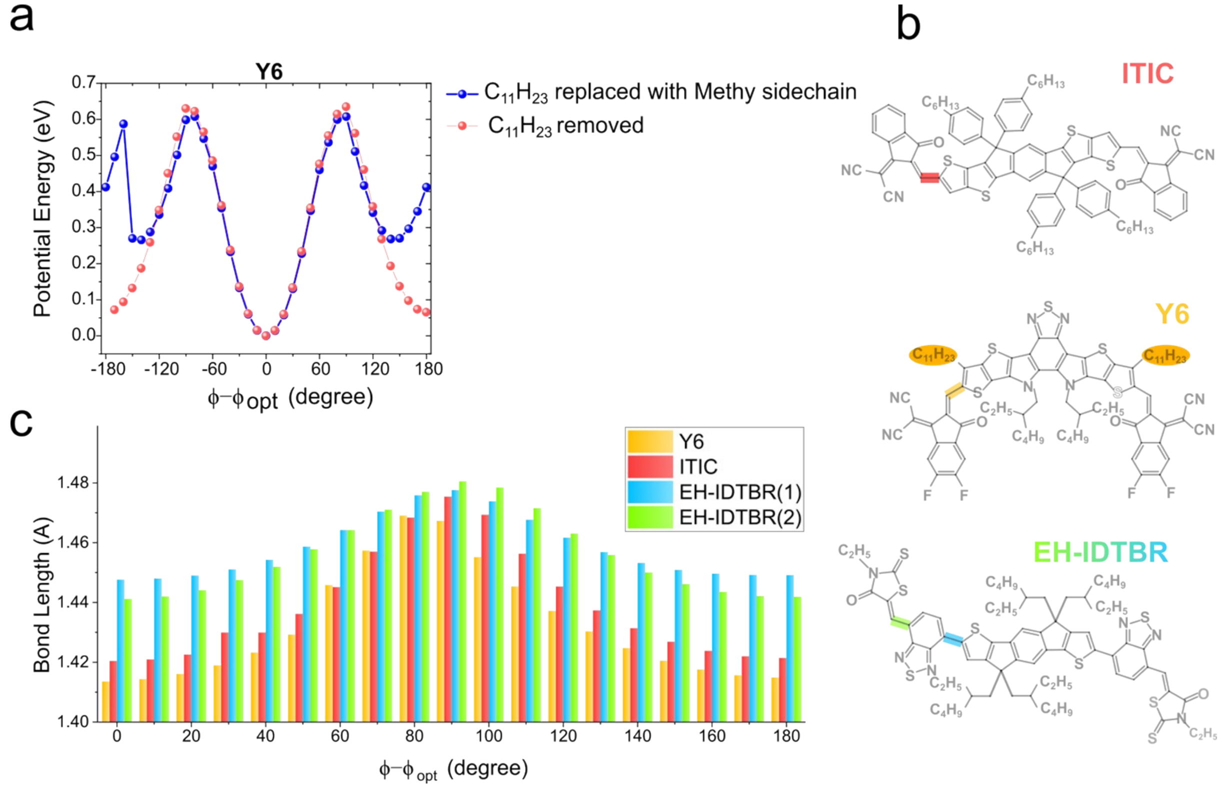

**Figure S3** (a) Relaxed dihedral potential scan for Y6 with $C_{11}H_{23}$, shown in orange ellipse in (b) replaced with methyl group as sidechain and without any $C_{11}H_{23}$ sidechain on the outer core of backbone. (c) Calculated bond length of the bridge for NF-SMAs in this study. The corresponding bond for each NF-SMAs is highlighted in (b).

## SI 9. Frontier Molecular Orbital contributing to the electronic transitions

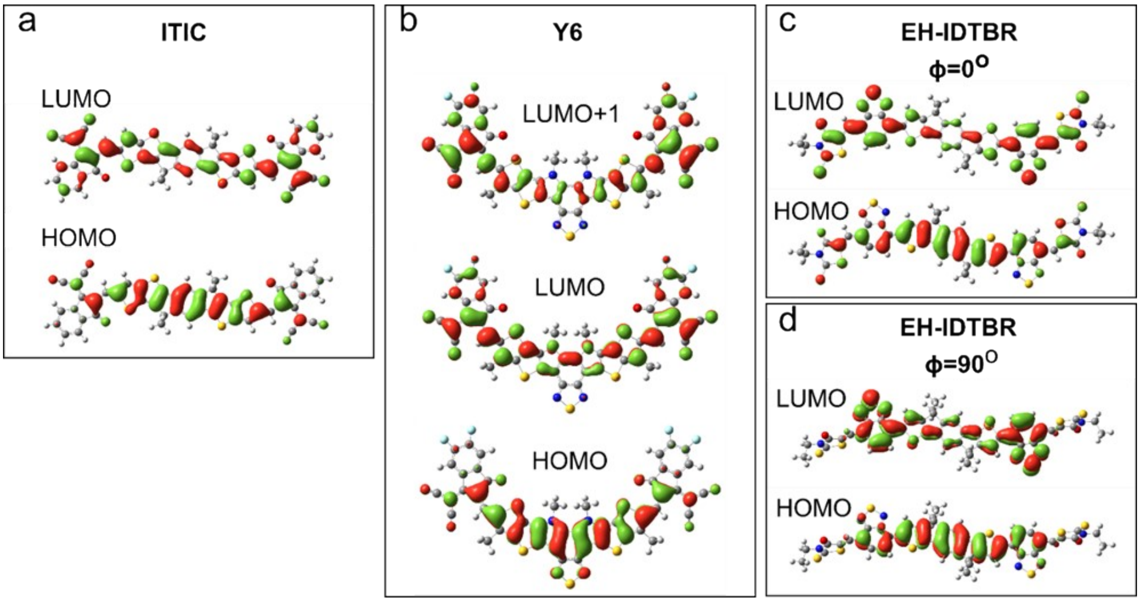

**Figure S4** Frontier Molecular Orbital contributing to the electronic transitions for (a) ITIC, (b) Y6 and (c) EH-IDTBR in the Ground state optimized geometry. (d) HOMO and LUMO of a conformation of EH-IDTBR with $\Phi_2 = 90^\circ$ for both end groups, are more localized compared to the conformation with $\Phi_2 = 0^\circ$.

### SI 10. TD-DFT calculation of $S_0 \rightarrow S_1$ excitation energy for EH-IDTBR at different dihedral angles.

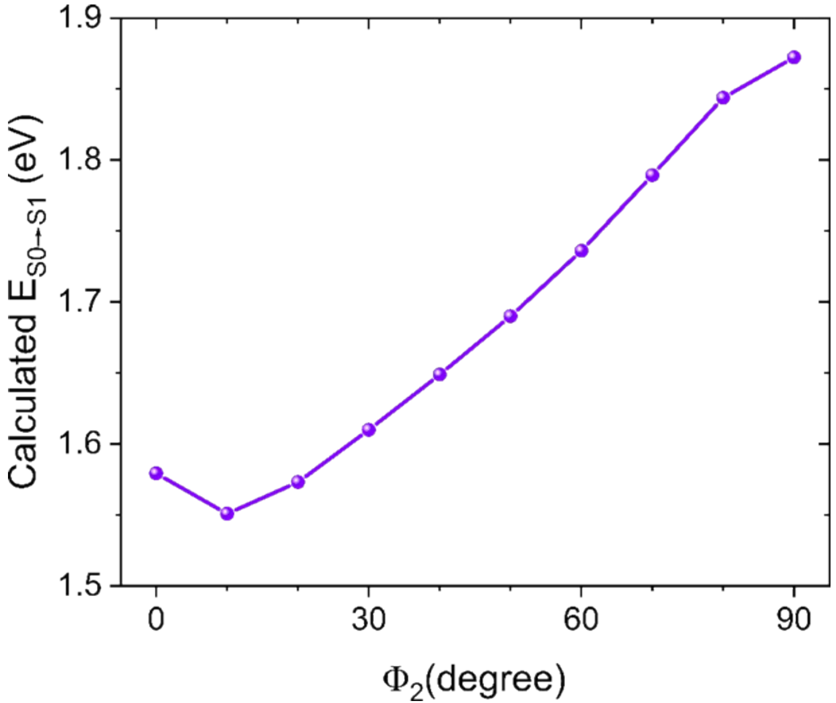

**Figure S5** TD-DFT calculation of $S_0 \rightarrow S_1$ excitation energy for EH-IDTBR at different rigid dihedral scans. Energy scans were constructed by changing the dihedral angle of optimized ground state structure.

## SI 11. DFT/TD-DFT Calculation of Intra-Molecular Relaxation Energy

Vertical Absorption calculation was done by DFT optimization of ground state geometry first and then TD-DFT energy calculation on the ground state geometry. The Vertical Emission calculation was done by TD-DFT optimization of first excited state geometry following with a TD-DFT energy calculation. The energy difference between Vertical Absorption and Vertical Emission is considered as an estimation for intra-molecular contribution into the Stokes-Shift. The solvent effects were taken into account using the Polarizable Continuum Model (PCM) model for CF. The side chains are replaced by methyl groups to reduce the computational time.

**Table S10** Vertical Absorption ($E^{vertical}_{abs}$) and Vertical emission ($E^{vertical}_{em}$) and intramolecular contribution into the Stokes Shift ($\Delta E^{intra}_{rel}$) of NF-SMAs calculated using DFT/TD-DFT.

| **NF-SMA** | **Experiment** | **B3LYP** | | | | **wB97XD** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\lambda^{intra}_{re}$ $(meV)$ | $E^{ve}$ $(eV$ | $E^{ve}$ $(eV$ | $\lambda^{in}$ $(me$ | **Error %** | $E^{vert}_{a}$ $(eV)$ | $E^{vert}_{e}$ $(eV)$ | $\lambda^{intr}_{re}$ $(me$ | **Error %** |
| $ITIC$ | 128 | 1.770 | 1.629 | 141 | 10% | 1.765 | 1.6258 | 139 | 8.6% |
| $Y6$ | 103 | 1.710 | 1.600 | 109 | 5.8% | 1.808 | 1.6485 | 160 | 55% |
| EH-IDTBR | 154 | 1.580 | 1.419 | 161 | 4.5% | 1.674 | 1.4615 | 213 | 38% |

## SI 12. Absorption and Emission Spectra of NF-SMAs at different concentrations

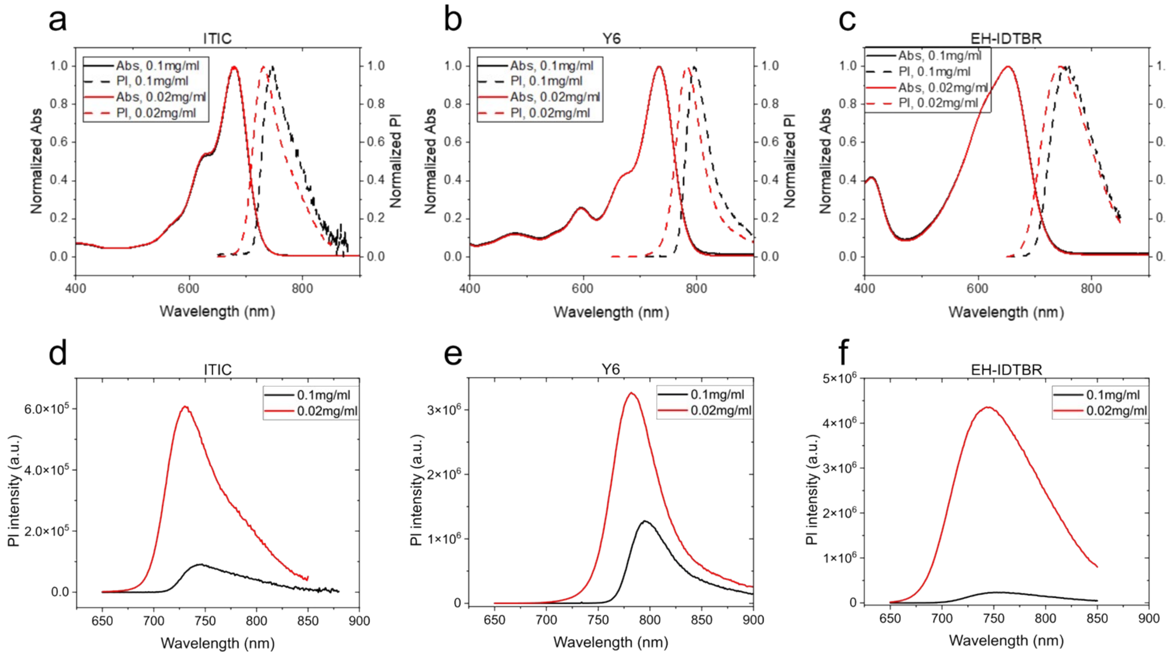

**Figure S6** The normalized absorption (Solid lines) and emission spectra (dashed lines) of representative of each group of NF-SMAs: a) ITIC, b) Y6 and c) EH-IDTBR in CF solution at different concentrations, 0.02mg/ml (red lines) and 0.1mg/ml (black lines). The effect of solution concentration on the photoluminescence intensity is shown figure d) for ITIC, e) Y6 and f) EH_IDTBR.

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