

## Supplementary Information

### **The structural and photophysical properties of multibranched derivatives with curved conjugated aromatic cores**

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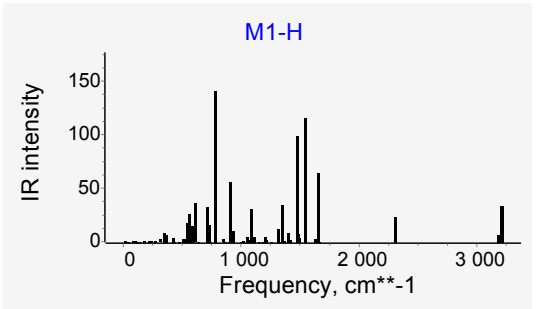
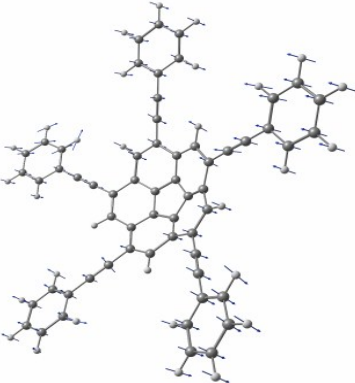
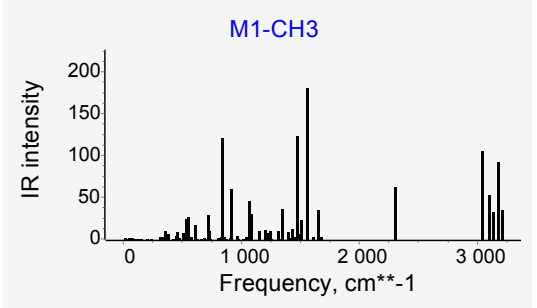
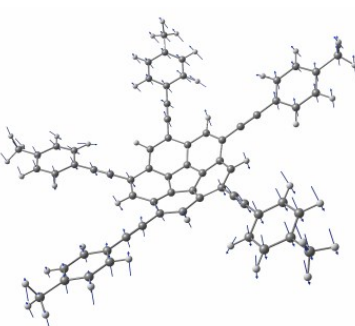
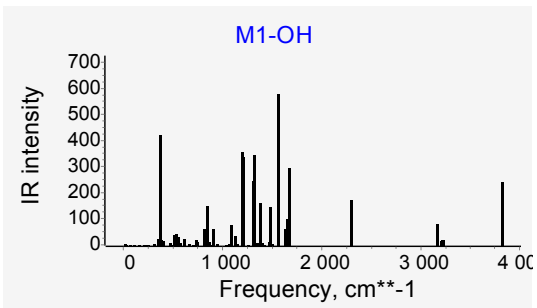
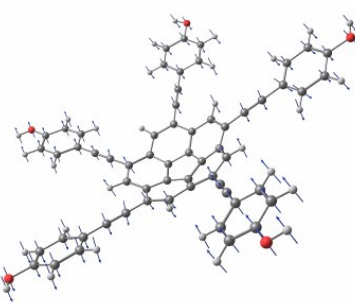
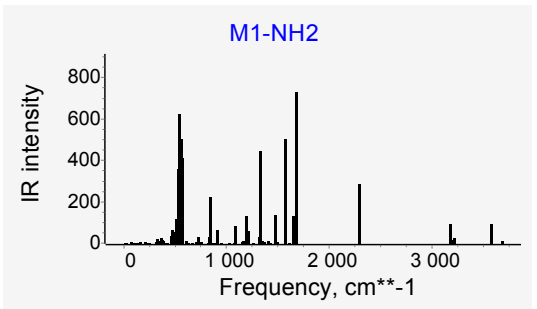
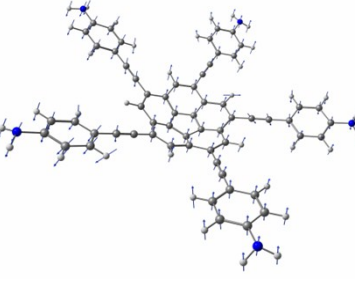
Table S1 the lowest ten vibrational frequencies and corresponding intensity of M1-R derivatives.

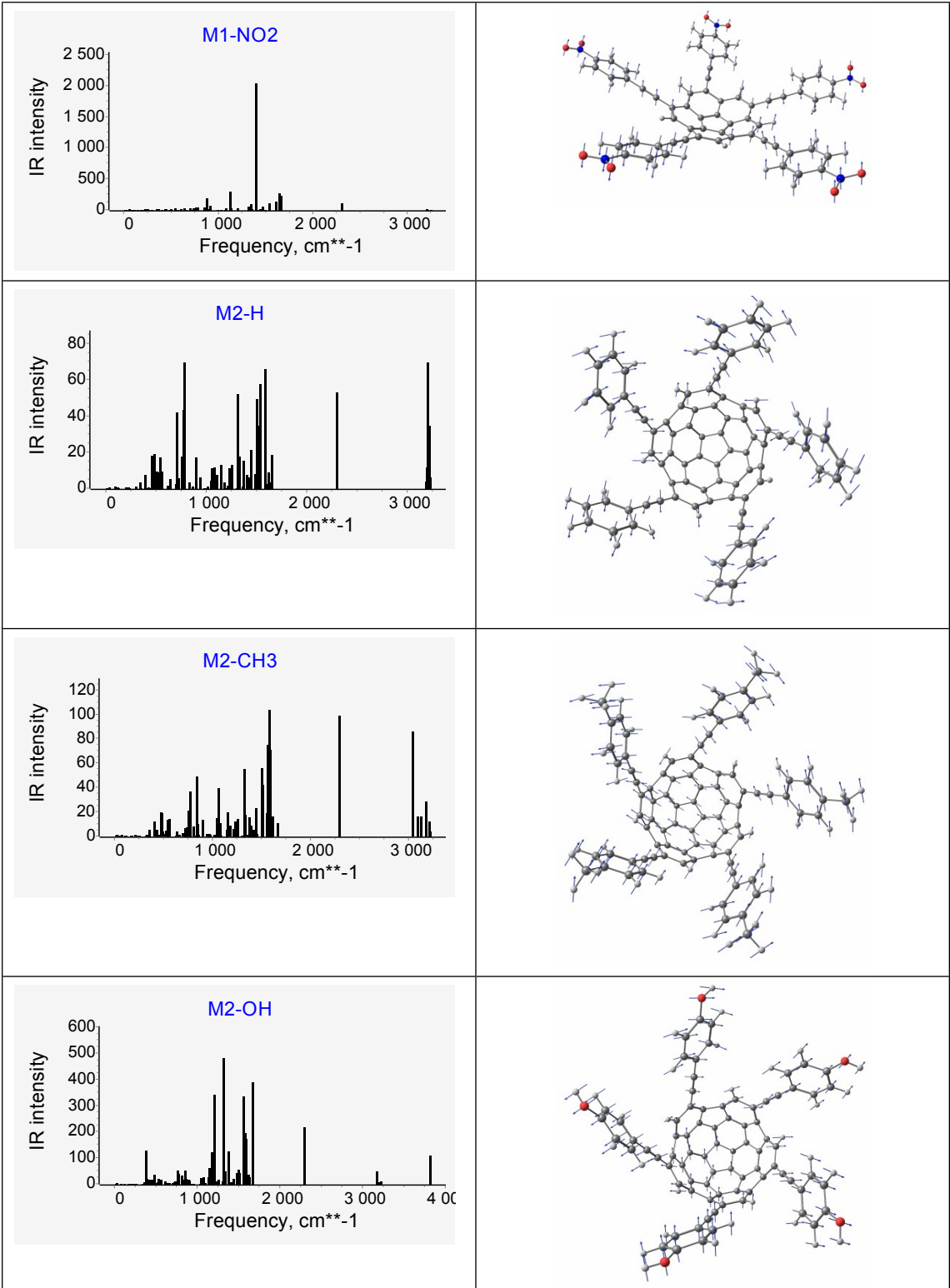
M1-H		M1-CH3		M1-OH		M1-NH2		M1-NO2	
10.0868	0.0007	8.4932	0	8.7734	0	8.0831	0.1686	6.3775	0.0022
10.2599	0.0015	8.4932	0	8.7734	0	8.5577	0.0007	6.567	0.0034
12.1128	0.0144	10.1245	0.078	11.9306	0	10.013	0.5615	8.2071	0.1791
13.1581	0.0313	10.1245	0.078	11.9306	0	10.9035	0.1082	9.3072	0.0392
14.5848	0.0206	10.385	0	12.1798	2.7339	12.3429	0.0216	9.6912	0.4701
15.1134	0.4128	10.385	0	12.5176	0.1508	12.6623	0.2304	10.1984	0.5408
15.4958	0.0046	10.5442	0.1394	12.5176	0.1508	13.2841	1.5145	10.42	0.716
15.9939	0.0256	13.1814	0.4597	15.5351	1.6263	13.9395	0.641	10.8752	0.4278
16.8296	0.0977	14.2989	0	16.2261	0.3563	14.7425	1.0614	12.0297	0.0503
17.3075	0.0671	14.2989	0	16.2261	0.3563	18.1896	0.3497	14.8405	0.0928

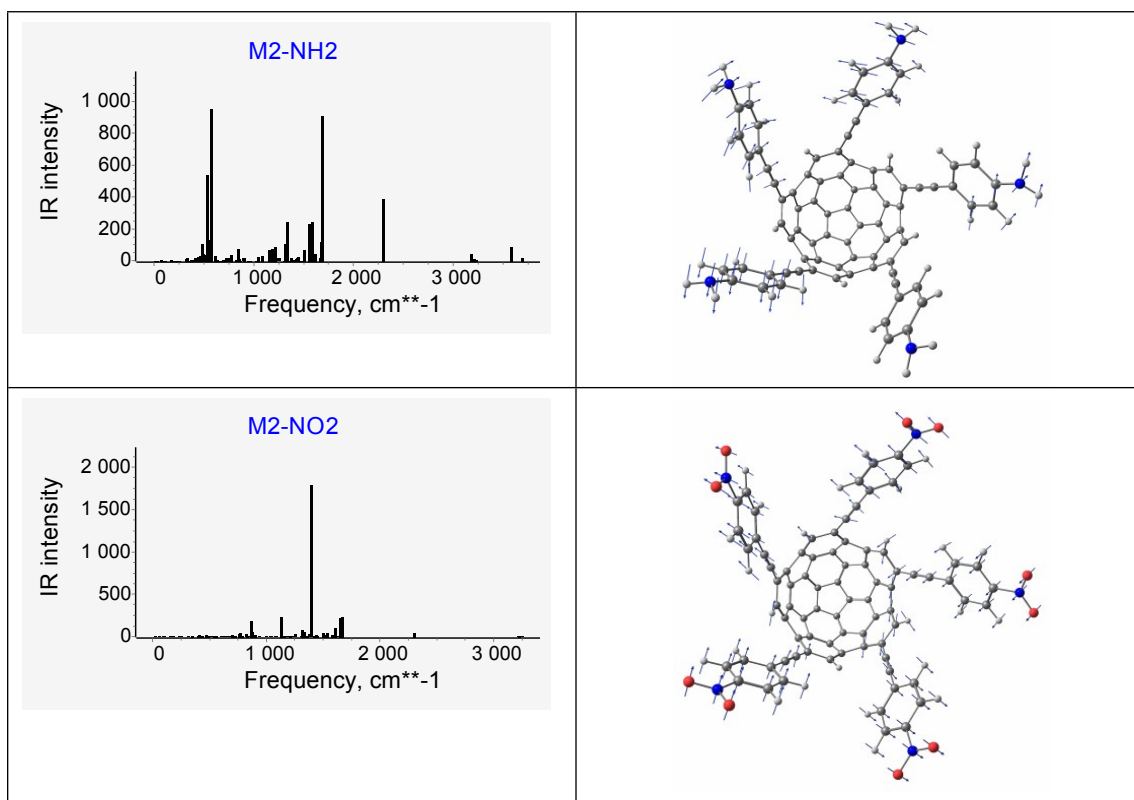
Table S2 the lowest ten vibrational frequencies and corresponding intensity of M2-R derivatives.

M2-H		M2-CH3		M2-OH		M2-NH2		M2-NO2	
7.442	0	5.8985	0.0014	7.6584	0.0255	5.0003	0.0424	6.2333	0.0028
7.442	0	7.4877	0.0066	8.4298	0.0032	6.4209	0.0144	6.4356	0.0066
9.5652	0.0011	7.9382	0.0115	8.9073	0.1256	7.3094	0.281	7.1215	0.0627
9.5652	0.0011	8.5686	0.0321	9.1503	0.0354	7.6271	0.0736	7.483	0.115
10.1108	0.0384	9.1228	0.0061	9.4056	0.1057	8.599	0.1126	7.6055	0.0799
12.1973	0	10.3329	0.0043	10.1473	0.0012	9.8593	0.0176	8.065	0.0305
12.1973	0	10.5854	0.0002	10.3116	0.0267	9.9541	0.0062	8.495	0.0209
23.6729	0	20.6572	0.0586	19.76	0.5788	20.2164	0.0053	15.9205	0.0857
23.6729	0	23.2807	0.1365	22.5245	0.565	22.6189	0.1817	17.4966	0.0169
25.2561	0.069	23.9047	0.2582	23.3248	0.3978	23.9697	0.9541	18.213	0.0722

Table S3 IR spectrum and corresponding normal vibrational mode of the lowest frequencies of M1-R and M2-R derivatives.

IR spectrum	Vibrational mode of lowest frequency
<p data-bbox="475 465 544 495">M1-H</p>  <p>The IR spectrum for M1-H shows IR intensity on the y-axis (0 to 150) and Frequency, cm<sup>-1</sup> on the x-axis (0 to 3000). Significant peaks are observed at approximately 1400, 1350, 1250, 1150, 1050, 950, 850, and 750 cm<sup>-1</sup>.</p>	 <p>A ball-and-stick model of the M1-H molecule showing the lowest frequency vibrational mode. The atoms are colored by element: carbon (grey), hydrogen (white), and oxygen (red).</p>
<p data-bbox="475 801 560 831">M1-CH3</p>  <p>The IR spectrum for M1-CH3 shows IR intensity on the y-axis (0 to 200) and Frequency, cm<sup>-1</sup> on the x-axis (0 to 3000). Significant peaks are observed at approximately 1400, 1350, 1250, 1150, 1050, 950, 850, 750, and a sharp peak at 3000 cm<sup>-1</sup>.</p>	 <p>A ball-and-stick model of the M1-CH3 molecule showing the lowest frequency vibrational mode. The atoms are colored by element: carbon (grey), hydrogen (white), and oxygen (red).</p>
<p data-bbox="475 1171 555 1200">M1-OH</p>  <p>The IR spectrum for M1-OH shows IR intensity on the y-axis (0 to 700) and Frequency, cm<sup>-1</sup> on the x-axis (0 to 4000). Significant peaks are observed at approximately 3400, 3000, 1600, 1500, 1400, 1350, 1250, 1150, 1050, 950, 850, and 750 cm<sup>-1</sup>.</p>	 <p>A ball-and-stick model of the M1-OH molecule showing the lowest frequency vibrational mode. The atoms are colored by element: carbon (grey), hydrogen (white), and oxygen (red).</p>
<p data-bbox="475 1507 560 1536">M1-NH2</p>  <p>The IR spectrum for M1-NH2 shows IR intensity on the y-axis (0 to 800) and Frequency, cm<sup>-1</sup> on the x-axis (0 to 3000). Significant peaks are observed at approximately 3400, 3000, 1600, 1500, 1400, 1350, 1250, 1150, 1050, 950, 850, and 750 cm<sup>-1</sup>.</p>	 <p>A ball-and-stick model of the M1-NH2 molecule showing the lowest frequency vibrational mode. The atoms are colored by element: carbon (grey), hydrogen (white), oxygen (red), and nitrogen (blue).</p>





The development of range-separated exchange (RS) density functionals has allowed the mitigation of the CT issue with TDDFT. As reported in recent work, TDDFT methods using conventional hybrid functionals surprisingly fail in describing the low-lying excited states. The description of excitonic properties for CT molecular systems requires the full 100% Hartree-Fock exchange and a reasonable long-range-separated parameter<sup>1,2</sup>. In this part, we compared the results (as shown in Table S4) from CAM-B3YP, M06-2x and a range-separated exchange density functionals with optimized range-separation parameter  $\omega$  and contribution of Hartree-Fock exchange. It is well known that the  $\omega$  values in RS functionals have been shown to be strongly system-dependent. In present calculation, the choice of parameter  $\omega$  is based on “Golden proportion” method recommended by Baer, Kronik, and their collaborators<sup>3</sup>

To facilitate functional tuning we employed a RS hybrid with a three-parameter error-function separation of the interelectronic distance  $r_{12}$  as follows

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta \text{erf}(\omega r_{12})]}{r_{12}} + \frac{\alpha + \beta \text{erf}(\omega r_{12})}{r_{12}}$$

The long-range component of the hybrid functional is given by the second term on the right-hand side. The switching from DFT-like to (HF-like) exact exchange (eX) is determined by the range-separation parameter  $\gamma$ . The procedure is designed such that  $\epsilon_H$  is as close as possible to the negative IP, which is an exact condition in Kohn–Sham (KS) and generalized KS theory, for both the N-electron and N+ 1 electron systems. The procedure produces H–L energy gaps that are optimally close to the fundamental gap IP–EA of the N-electron system.

$$J^2 = \sum_{i=0}^1 [\varepsilon_H(N+i) + IP(N+i)]^2$$

Here, N is the electron number of the system,  $\varepsilon_H$  is the HOMO energy, and IP is the ionization potential calculated from self-consistentfield (SCF) energy differences.

The optimal  $\omega$  values are in the range from 0.126 to 0.129 Bohr<sup>-1</sup> for M1-R systems, The optimal  $\omega$  values of M2-R range from 0.217 to 0.221 Bohr<sup>-1</sup>. They are thus significantly smaller than the default  $\omega$  value for LC- $\omega$ PBE, CAM-B3LYP and M062x ). In order to compare the behavior of various functionals, some excited state datum are listed in Table S2. The untuned RS functionals, such as CAM-B3LYP and M062x, produce slightly greater errors compared to experimental results. the allowed maximum absorption wavelengths ( $\lambda_{\max}$ ) of M1-NH<sub>2</sub> predicted by CAM-B3LYP and M062x consistently are overestimated by percentages 15.0 and 14.3%, respectively. The predicted  $\lambda_{\max}$  using optimal LC- $\omega$ PBE functionals is agree with the experiment data, only a small deviation less than 4nm. If Optimal LC- $\omega$ PBE results are regarded as a benchmark, similar tendency was also observed in the multibranching corannulene with acceptor ends, M1-NO<sub>2</sub>.

Table S4 Comparison of excited properties predicted using various functionals.

	M1-NH <sub>2</sub>	M1-NO <sub>2</sub>
IP	-6.088098	-7.468587
EA	1.174446	2.348647
Gap	4.889344	5.089620
J2	0.004920	0.000112
$\omega$	0.1262	0.1291
$\lambda_{\max}$ -LC- $\omega$ PBE	416.8	405.5
$\lambda_{\max}$ -CAM-B3LYP	355.6	347.5
$\lambda_{\max}$ -M062X	360.4	346.9
$\lambda_{\max}$ -experiment	420.0	-

(1) B. M. Wong, T. H. Hsieh, Optoelectronic and Excitonic Properties of Oligoacenes: Substantial Improvements from Range-Separated Time-Dependent Density Functional Theory, *J. Chem. Theory Comput.* 2010, 6,3704–3712

(2) T. Seidler, K. Stadnicka, B. Champagne, Evaluation of the Linear and Second-Order NLO Properties of Molecular Crystals within the Local Field Theory: Electron Correlation Effects, Choice of XC Functional, ZPVA Contributions, and Impact of the Geometry in the Case of 2-Methyl-4-nitroaniline, *J. Chem. Theory Comput.* 2014, 10, 2114–2124.

(3) R. Baer, E. Livshits, U.Salzner, Tuned Range-Separated Hybrids in Density Functional Theory, *Annu. Rev. Phys. Chem.* 2010, 61,85–109

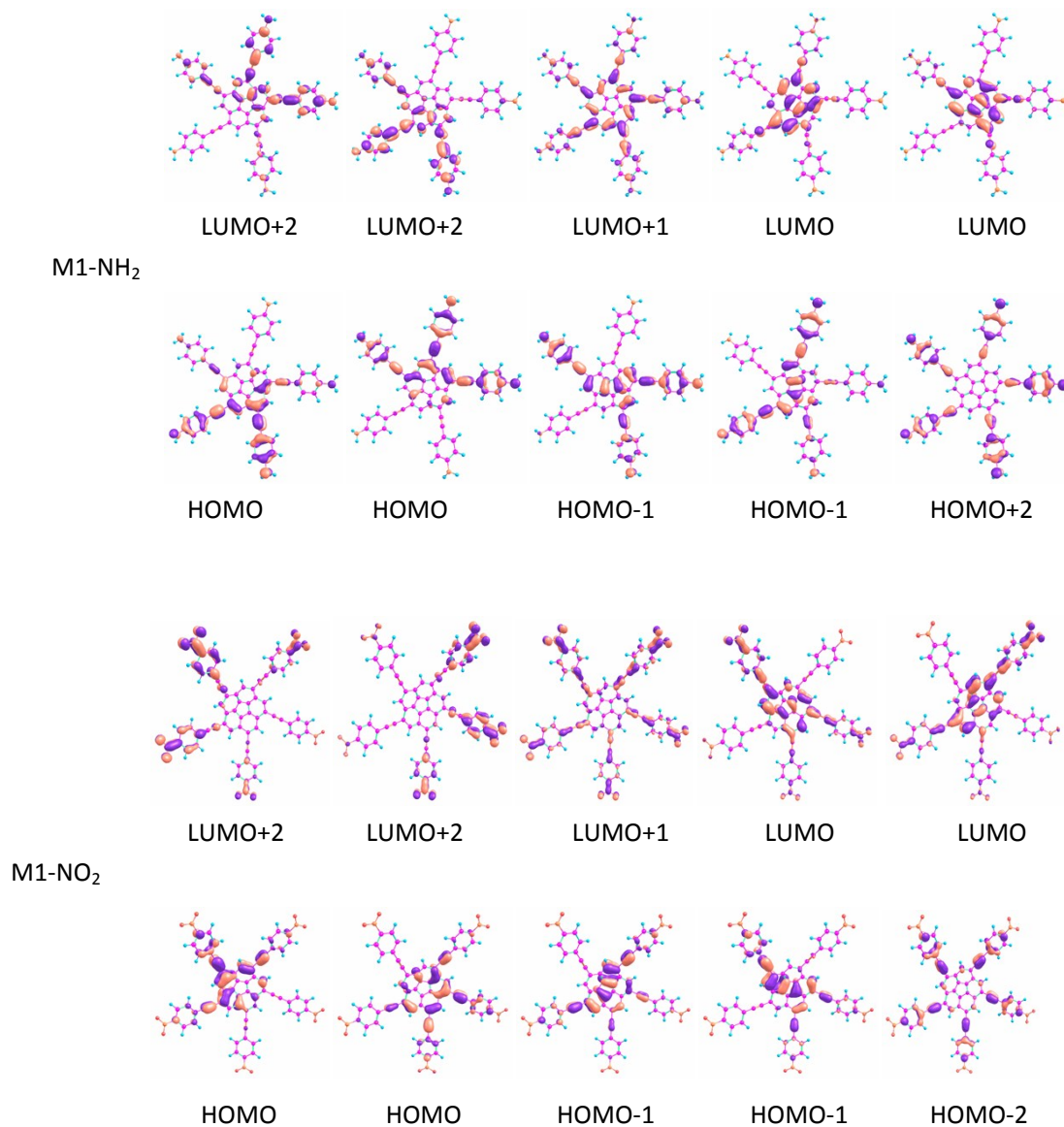


Fig S1 Molecular orbital diagrams of M1-NH<sub>2</sub> and M1-NO<sub>2</sub> calculated at the B3LYP/6-31+G(d,p) level of theory.

Note: The front molecular orbital diagrams of M1-H, M1-CH<sub>3</sub>, M1-OH have similar electron density distribution to that of M1-NH<sub>2</sub>.

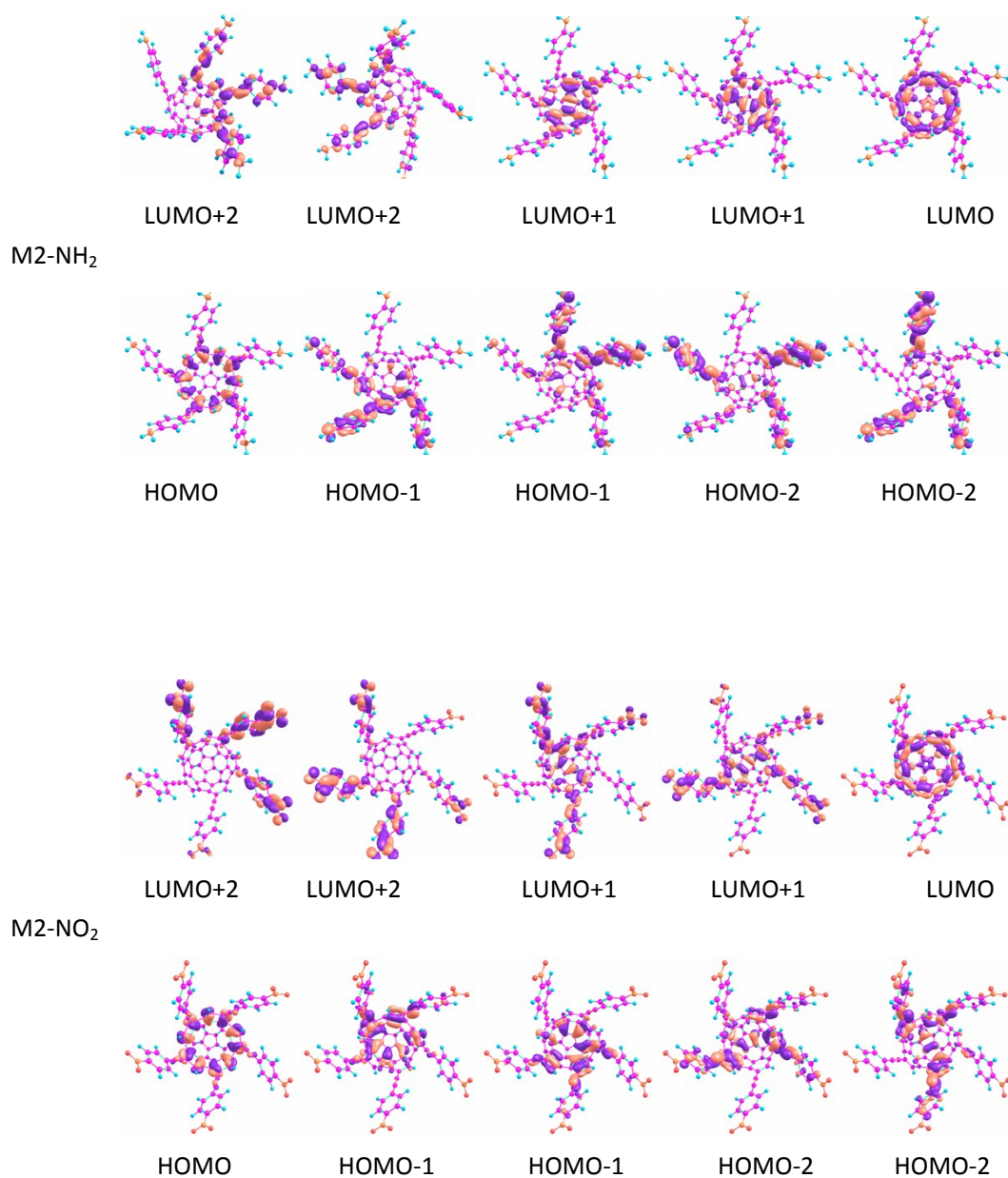


Fig S2 Molecular orbital diagrams of M2-NH<sub>2</sub> and M2-NO<sub>2</sub> calculated at the B3LYP/6-31+G(d,p) level of theory.

Note: The front molecular orbital diagrams of M2-H, M2-CH<sub>3</sub>, M2-OH have similar electron density distribution to that of M2-NH<sub>2</sub>.



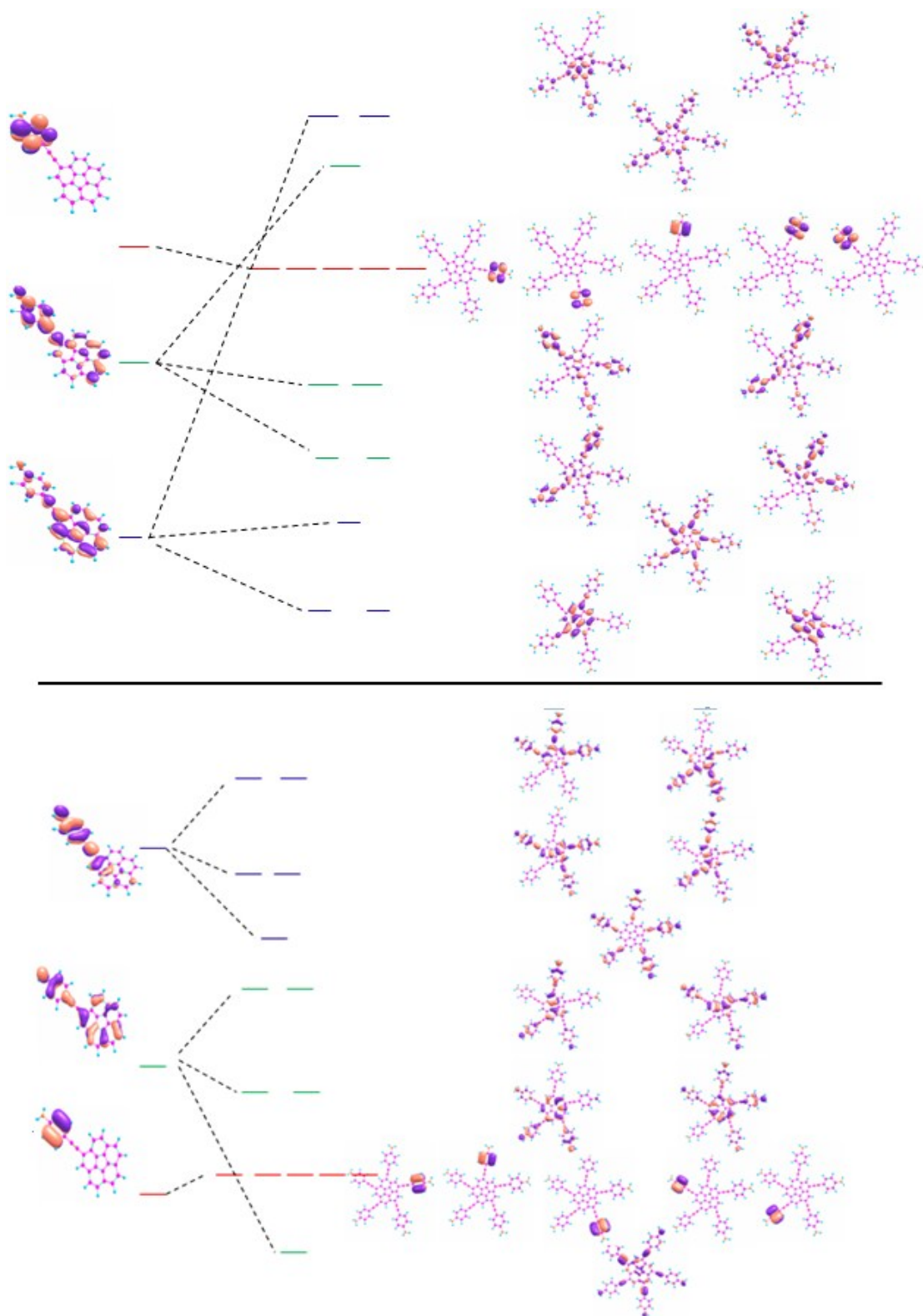


Fig S3 Orbital correlation diagram from single branched to multibranched corannulene derivative.