# *Supporting Information for*

# Negative isotope effect for charge transport in acenes and derivatives – A theoretical conclusion

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## 1. Discussion on the reorganization energy difference between hole and electron transfer contributed by Mode 1.

The normal modes coordinates of two electronic states $\mathbf{Q}_i$ and $\mathbf{Q}_f$ can be related by a Duschinsky rotation matrix $S_{i\leftarrow f}$ and a coordinate displacement vector $D_{i\leftarrow f}$:

$$\mathbf{Q}_i = \mathbf{S}_{i\leftarrow f}\mathbf{Q}_f + \mathbf{D}_{i\leftarrow f} \tag{S1}$$

where

$$\mathbf{S}_{i\leftarrow f} = \mathbf{L}_i^T\mathbf{L}_f \tag{S2}$$

and

$$\mathbf{D}_{i\leftarrow f} = \mathbf{L}_i^T\mathbf{M}^{1/2}(\mathbf{R}_{f0} - \mathbf{R}_{i0}) \tag{S3}$$

Here the Duschinsky rotation matrix $S_{i\leftarrow f}$ is a unitary matrix, whose elements represent the mixing of normal modes in the initial and final electronic states. $D_{i\leftarrow f}$ is a displacement vector connecting the minima of the parabolas of the two electronic states. $\mathbf{L}_i$ is the eigenvectors of Hessian matrix of the initial electronic state. Therefore, with the eigenvectors of Hessian matrix $\mathbf{L}$ and equilibrium geometry coordinates $\mathbf{R}_{i(f)}$ achieved from Quantum chemistry computation, the displacement along *k*-th normal mode between the equilibrium positions of

charged state and neutral state $\Delta Q_k$ can be obtained.

For most cases in rigid molecules, there is nearly no Duschinsky mixing so that the two electronic states can be characterized by the same force constants,[1, 2] thus eqn (S3) can be simplified as

$$\mathbf{Q}_{\mathrm{i}} - \mathbf{Q}_{\mathrm{f}} = \mathbf{L}_{\mathrm{i}}^{\mathrm{T}}\mathbf{M}^{1/2}(\mathbf{R}_{\mathrm{f}0} - \mathbf{R}_{\mathrm{i}0}) \tag{S4}$$

Therefore, the normal mode displacement can be related to electronic state structure displacement by Hessian matrix.

The reorganization energy can also be written as

$$\lambda = \sum_i \lambda_i = \sum_j \frac{V_i^2}{2\omega_i^2} \tag{S5}$$

where $V_i$ is the vibronic coupling constant for mode $i$:

$$V_i = \left\langle \Psi^{\pm}(\mathbf{r},\mathbf{R_0}) \left| \left( \frac{\partial H(\mathbf{r},\mathbf{R})}{\partial Q_i} \right)_{\mathbf{R_0}} \right| \Psi^{\pm}(\mathbf{r},\mathbf{R_0}) \right\rangle \tag{S6}$$

Here, $\Psi^{\pm}(\mathbf{r},\mathbf{R_0})$ is the wavefunction of the cation (anion) state at the optimal geometry ($\mathbf{R_0}$) of the neutral state. By making use of Koopman's theorem approximation, namely by replacing the total energy of the charged molecule with the energy of the relevant frontier molecular orbital, the hole (electron) vibronic coupling constant can be expressed as

$$V_i = \frac{\partial E_{HOMO(LUMO)}}{\partial Q_i} \tag{S7}$$

According to eqn (S4), the contribution to reorganization energy by **Mode 1** is related to the equilibrium geometry difference between neutral and cation/anion states (Fig. S1). It is easy to find that, for that low frequency mode, all the carbon atoms on one side of the $\sigma_{yz}$ mirror move in the same direction along the $x$ axis, which identifies with the displacement from neutral state to anion state. Since the $k$-th eigenvector of Hessian matrix $\mathbf{L}_{\mathrm{k,i(f)}}$ determines the $k$-th normal mode coordinates $\mathbf{Q}_{\mathrm{k,i(f)}}$, the same/opposite direction between the normal mode displacements $\mathbf{Q}_{\mathrm{k,i(f)}}$ and the electronic structure change between two states $\mathbf{R}_{\mathrm{f}0}$-$\mathbf{R}_{\mathrm{i}0}$ can lead to the large displacement $\Delta\mathrm{Q_k}$ along $k$th normal mode coordinate between charged state and neutral state, and then result in large Huang-Rhys factor and reorganization energy. Thus, **Mode 1** makes a considerable contribution to reorganization energy in electron

transport, and shows nearly no contribution in hole transport.

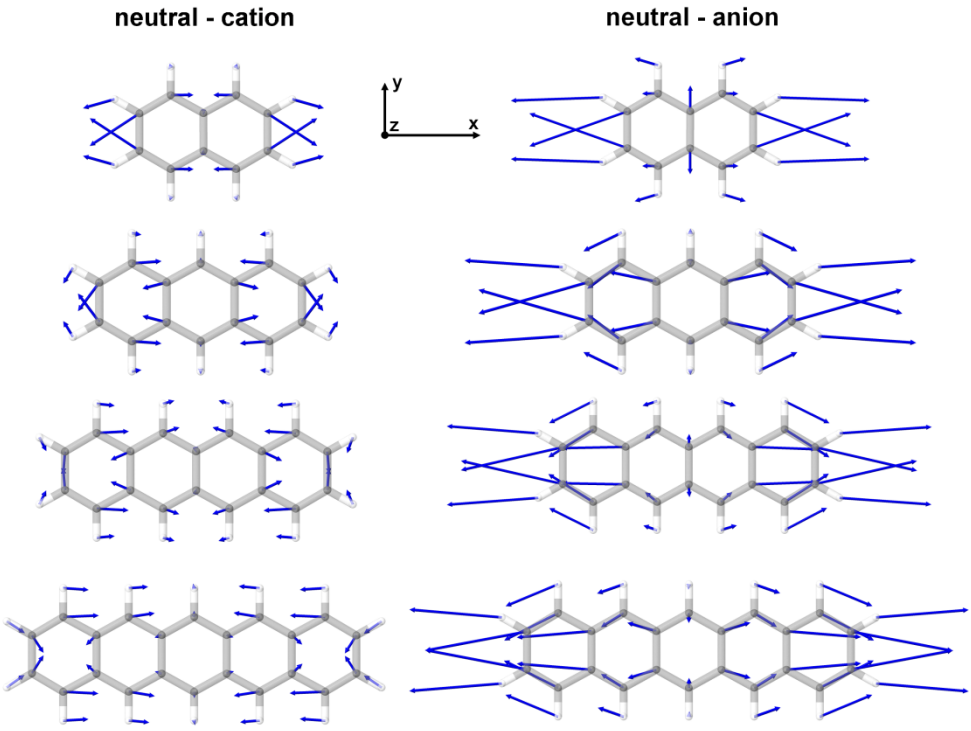


**Fig. S1** The displacements from neutral equilibrium geometry to cation (anion) equilibrium geometry for acenes.

Moreover, the hole (electron) reorganization energy contributed by **Mode 1** is directly determined by the electronic distributions of HOMO (LUMO) according to eqn (S5) and (S7). For one mode, $\lambda_i^e/\lambda_i^h = \left(\frac{\delta E_{LUMO}}{\delta Q_i}/\frac{\delta E_{HOMO}}{\delta Q_i}\right)^2$. The numerical calculation results for **Mode 1** listed in Table S1 indicate that **Mode 1** indeed causes much larger change on the electronic structure of LUMO than HOMO. The HOMO and LUMO patterns presented in Fig. S2 can serve a good illustration on that numerical result. For all acenes, the number of nodal planes of HOMO is less than that of LUMO. Therefore, when one acene is distorted along **Mode 1** toward the direction as shown in Fig. 2, the anti-bonding interaction in LUMO become stronger than that in HOMO, and the bonding interaction changes little in both HOMO and LUMO since the bond length is nearly unchanged in **Mode 1**. Thus, LUMO energy changes more than HOMO energy along **Mode 1**, then leading to stronger electron-phonon coupling than hole-phonon coupling.

**Table S1** The numerical results of $\left(\frac{\delta E_{LUMO}}{\delta Q_i}/\frac{\delta E_{HOMO}}{\delta Q_i}\right)^2$ for **Mode 1** for acenes.

| **compounds** | **naphthalene** | **anthracene** | **tetracene** | **pentacene** |
|---|---|---|---|---|
| $\left(\frac{\delta E_{LUMO}}{\delta Q_i}/\frac{\delta E_{HOMO}}{\delta Q_i}\right)^2$ | 17.11 | 200.17 | 41.74 | 9.04 |

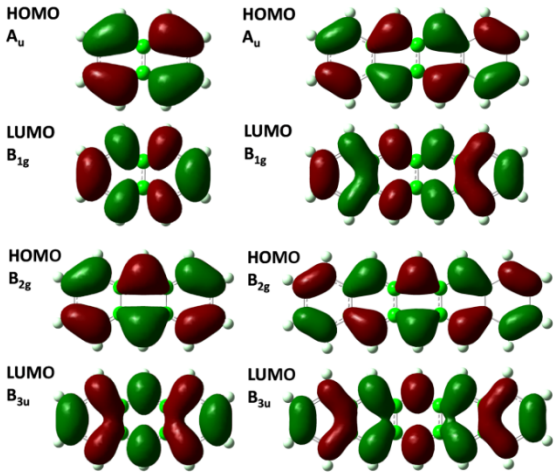


**Fig. S2** Orbital patterns of HOMOs and LUMOs of acenes.

## 2. The normal mode analysis for naphthalene, anthracene, tetracene, pentacene and their corresponding derivatives.

**Table S2** The frequencies ($\omega$), Huang-Rhys factors ($S$), reorganization energies ($\lambda$), and vibration types of all vibrational modes with $\lambda > 1$ meV for neutral acenes in both hole an electron transport processes.

| Compd. | Hole | | | | Electron | | | |
|---|---|---|---|---|---|---|---|---|
| | $\omega$ (cm$^{-1}$) | $S$ | $\lambda$ (meV) | vib.[a] | $\omega$ (cm$^{-1}$) | $S$ | $\lambda$ (meV) | vib.[a] |
| **naphthalene** | 1630.48 | 0.2676 | 54.10 | i, ii | 1417.37 | 0.3162 | 55.57 | ii |
| | 1417.37 | 0.1762 | 30.96 | ii | 1630.48 | 0.1911 | 38.63 | i, ii |
| | 1509.40 | 0.0239 | 4.47 | i, ii | 520.61 | 0.4431 | 28.60 | iii |
| | 1194.16 | 0.0281 | 4.16 | i | 1194.16 | 0.0440 | 6.51 | i |
| | 520.61 | 0.0474 | 3.06 | iii | 776.52 | 0.0466 | 4.49 | iii |
| **anthracene** | 1609.66 | 0.1984 | 39.59 | i, ii | 1444.70 | 0.1896 | 33.96 | ii |
| | 1444.70 | 0.0950 | 17.01 | ii | 398.90 | 0.5526 | 27.33 | iii |
| | 1303.56 | 0.0514 | 8.30 | i, ii | 1609.66 | 0.0975 | 19.46 | i, ii |
| | 1199.56 | 0.0220 | 3.27 | i | 1303.56 | 0.0655 | 10.59 | i, ii |
| | 1535.11 | 0.0103 | 1.96 | i, ii | 1199.56 | 0.0376 | 5.59 | i |
| | | | | | 642.20 | 0.0298 | 2.37 | iii |
| **tetracene** | 1593.89 | 0.1257 | 24.84 | i, ii | 318.52 | 0.5636 | 22.26 | iii |
| | 1428.24 | 0.0656 | 11.61 | i, ii | 1428.24 | 0.0929 | 16.45 | i, ii |
| | 1239.18 | 0.0481 | 7.39 | i, ii | 1442.28 | 0.0715 | 12.78 | i, ii |
| | 1442.28 | 0.0333 | 5.95 | i, ii | 1593.89 | 0.0490 | 9.68 | i, ii |
| | 1574.12 | 0.0282 | 5.51 | i, ii | 1239.18 | 0.0604 | 9.28 | i, ii |
| | 1195.38 | 0.0108 | 1.60 | i | 634.61 | 0.0485 | 3.81 | iii |
| | 1497.80 | 0.0077 | 1.42 | i, ii | 1195.38 | 0.0211 | 3.13 | i |
| | | | | | 1497.80 | 0.0120 | 2.23 | i, ii |
| **pentacene** | 1572.08 | 0.0903 | 17.60 | i, ii | 1426.21 | 0.1055 | 18.65 | i, ii |
| | 1426.21 | 0.0750 | 13.25 | i, ii | 264.13 | 0.5490 | 17.98 | iii |
| | 1222.72 | 0.0496 | 7.51 | i | 1222.72 | 0.0593 | 8.98 | i |
| | 1451.15 | 0.0130 | 2.33 | i, ii | 1451.15 | 0.0349 | 6.28 | i, ii |
| | 1593.67 | 0.0115 | 2.26 | i, ii | 616.64 | 0.0449 | 3.43 | iii |
| | 1194.24 | 0.0088 | 1.31 | i | 1572.08 | 0.0170 | 3.31 | i, ii |
| | | | | | 1194.24 | 0.0164 | 2.43 | i |
| | | | | | 765.28 | 0.0150 | 1.43 | ii, iii |
| | | | | | 1593.67 | 0.0057 | 1.12 | i, ii |

[a] Vibration types: (i) in-plane bending vibration of aromatic H (Ar–H); (ii) aromatic ring stretching vibration; (iii) aromatic ring in-plane bending vibration; (iv) C–N stretching vibration; (v) C=O stretching vibration; (vi) out-of-plane bending vibration of Ar-H; (vii) aromatic ring out-of-plane bending vibration; (viii) the rocking/wagging vibrations of $–CH_2–$ and $–CH_3$ in the side chain (namely, $–CH_2–$ or $–CH_3$ is vibrating as a whole); (ix) $–CH_2–$ or $–CH_3$ deformation vibration. The major contributed vibration type of each mode is underlined.

**Table S3** The frequencies ($\omega$), Huang-Rhys factors ($S$), reorganization energies ($\lambda$), and vibration types of all vibrational modes with $\lambda > 1$ meV for five neutral acene derivatives in both hole an electron transport processes.

| Compd. | Hole | | | | Electron | | | |
|---|---|---|---|---|---|---|---|---|
| | $\omega$ (cm$^{-1}$) | $S$ | $\lambda$ (meV) | Vibration types[a] | $\omega$ (cm$^{-1}$) | $S$ | $\lambda$ (meV) | Vibration types[a] |
| **1** | 1671.05 | 0.0538 | 11.15 | i, ii (anthracene), ii (phenyl) | 1656.07 | 0.1015 | 20.85 | i, ii (anthracene), ii (phenyl) |
| | 1656.07 | 0.0508 | 10.42 | i, ii (anthracene), ii (phenyl) | 1213.34 | 0.1096 | 16.49 | i, ii (anthracene) |
| | 1601.48 | 0.0472 | 9.37 | i, ii (anthracene) | 1456.49 | 0.0588 | 10.62 | ii (anthracene) |
| | 1213.34 | 0.0521 | 7.84 | i, ii (anthracene) | 1671.05 | 0.0484 | 10.02 | i, ii (anthracene), ii (phenyl) |
| | 144.52 | 0.4149 | 7.43 | iii (anthracene) | 144.52 | 0.4292 | 7.69 | iii (anthracene) |
| | 1701.85 | 0.0324 | 6.83 | i, ii (anthracene), ii (phenyl), C=C stretching | 1701.85 | 0.0201 | 4.25 | i, ii (anthracene), ii (phenyl), C=C stretching |
| | 1456.49 | 0.0330 | 5.96 | ii (anthracene) | 1601.48 | 0.0152 | 3.01 | i, ii (anthracene) |
| | 628.86 | 0.0471 | 3.68 | iii (anthracene), iii (phenyl) | 1398.72 | 0.0163 | 2.83 | i, ii (anthracene) |
| | 426.10 | 0.0359 | 1.90 | iii (anthracene), iii (phenyl) | 1527.33 | 0.0138 | 2.62 | i, ii (anthracene) |
| | 1381.99 | 0.0110 | 1.89 | i (anthracene), i (phenyl) | 209.63 | 0.0994 | 2.58 | iii (anthracene), iii (phenyl) |
| | 1327.75 | 0.0111 | 1.83 | i, ii (anthracene) | 1632.08 | 0.0123 | 2.48 | i, ii (phenyl) |
| | 1632.08 | 0.0086 | 1.73 | i, ii (phenyl) | 501.70 | 0.0395 | 2.46 | iii (anthracene), iii (phenyl) |
| | 1356.60 | 0.0088 | 1.47 | i, ii (anthracene), ii (phenyl), C=C stretching | 1381.99 | 0.0113 | 1.94 | i (anthracene), i (phenyl) |
| | 1160.82 | 0.0077 | 1.10 | i, ii (anthracene) | 1304.36 | 0.0096 | 1.56 | i, ii (anthracene) |
| | 520.51 | 0.0165 | 1.07 | iii (anthracene), iii (phenyl) | 1497.66 | 0.0081 | 1.50 | i, ii (phenyl) |
| | 1218.02 | 0.0071 | 1.07 | i (anthracene), i (phenyl) | 520.51 | 0.0220 | 1.42 | iii (anthracene), iii (phenyl) |
| | | | | | 876.34 | 0.0122 | 1.32 | iii (phenyl) |
| | | | | | 1327.75 | 0.0067 | 1.09 | i, ii (anthracene) |
| **2** | 1605.28 | 0.0798 | 15.88 | i, ii (anthracene) | 1258.38 | 0.1164 | 18.17 | i, ii (anthracene), ii (phenyl) |
| | 1258.38 | 0.0695 | 10.84 | i, ii (anthracene), ii (phenyl) | 2279.85 | 0.0551 | 15.57 | C≡C stretching |
| | 2279.85 | 0.0380 | 10.75 | C≡C stretching | 398.71 | 0.2973 | 14.70 | iii (anthracene) |
| | 1352.09 | 0.0462 | 7.75 | i, ii (anthracene), ii (phenyl) | 1605.28 | 0.0703 | 14.00 | i, ii (anthracene) |
| | 170.32 | 0.3444 | 7.27 | iii (anthracene) | 1352.09 | 0.0430 | 7.20 | i, ii (anthracene), ii (phenyl) |
| | 1528.59 | 0.0341 | 6.45 | i, ii (anthracene), ii (phenyl) | 1528.59 | 0.0331 | 6.27 | i, ii (anthracene), ii (phenyl) |
| | 538.33 | 0.0497 | 3.32 | iii (anthracene), iii (phenyl) | 682.27 | 0.0474 | 4.01 | iii (anthracene) |
| | 1203.40 | 0.0136 | 2.03 | i (anthracene) | 1203.40 | 0.0228 | 3.40 | i (anthracene) |
| | 1212.11 | 0.0100 | 1.50 | i (phenyl) | 1657.76 | 0.0161 | 3.31 | i, ii (phenyl) |
| | | | | | 1081.38 | 0.0105 | 1.40 | i, ii, iii (anthracene) |
| | | | | | 1015.34 | 0.0089 | 1.12 | iii (phenyl) |
| | | | | | 1051.18 | 0.0082 | 1.07 | i, ii, iii (anthracene) |
| **3** | 1587.60 | 0.0924 | 18.18 | i, ii | 1400.00 | 0.1104 | 19.16 | i, ii |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1543.62 | 0.0665 | 12.72 | i, ii | 327.52 | 0.4530 | 18.40 | iii |
| | 1400.00 | 0.0408 | 7.08 | i, ii | 1418.47 | 0.0513 | 9.01 | i, ii |
| | 956.13 | 0.0524 | 6.22 | ii, C-Cl stretching | 1587.60 | 0.0386 | 7.59 | i, ii |
| | 1235.99 | 0.0350 | 5.37 | i, ii | 1282.44 | 0.0272 | 4.33 | i, ii |
| | 1418.47 | 0.0305 | 5.36 | i, ii | 858.69 | 0.0388 | 4.13 | iii, C-Cl stretching |
| | 412.12 | 0.0569 | 2.91 | iii | 935.0 | 0.0320 | 3.71 | ii, iii, C-Cl stretching |
| | 1282.44 | 0.0142 | 2.26 | i, ii | 412.12 | 0.0668 | 3.41 | iii |
| | 1201.26 | 0.0144 | 2.14 | i | 1201.26 | 0.0199 | 2.96 | i |
| | 1486.70 | 0.0098 | 1.81 | i, ii | 956.13 | 0.0198 | 2.35 | ii, iii, C-Cl stretching |
| | | | | | 1485.14 | 0.0110 | 2.02 | i, ii |
| | | | | | 1543.62 | 0.0100 | 1.92 | i, ii |
| | | | | | 644.62 | 0.0237 | 1.90 | iii |
| | | | | | 213.87 | 0.0678 | 1.80 | iii |
| | | | | | 1235.99 | 0.0087 | 1.34 | i, ii |
| | | | | | 1486.70 | 0.0059 | 1.09 | i, ii |
| **4** | 1519.51 | 0.0949 | 17.88 | i, ii | 1357.41 | 0.1439 | 24.22 | ii |
| | 1357.41 | 0.0981 | 16.52 | ii | 365.09 | 0.3792 | 17.17 | iii, vii |
| | 1587.02 | 0.0587 | 11.55 | i, ii | 923.11 | 0.1337 | 15.30 | iii, vii |
| | 990.80 | 0.0659 | 8.09 | ii, vi | 1286.56 | 0.0402 | 6.42 | i, ii |
| | 309.88 | 0.1368 | 5.25 | iii, vii | 255.62 | 0.1723 | 5.46 | iii |
| | 923.11 | 0.0404 | 4.62 | iii, vii | 1587.02 | 0.0268 | 5.27 | i, ii |
| | 424.60 | 0.0630 | 3.32 | vii | 1205.67 | 0.0301 | 4.50 | i, ii |
| | 365.09 | 0.0660 | 2.99 | iii, vii | 1519.51 | 0.0203 | 3.82 | i, ii |
| | 170.28 | 0.1091 | 2.30 | vii | 424.60 | 0.0344 | 1.81 | vii |
| | 1464.95 | 0.0088 | 1.60 | i, ii | 1464.95 | 0.0066 | 1.20 | i, ii |
| **5** | 1564.19 | 0.0635 | 12.31 | i, ii | 263.50 | 0.4596 | 15.01 | iii, viii |
| | 1238.93 | 0.0695 | 10.68 | i, ii | 672.35 | 0.1183 | 9.86 | iii, C-Si stretching |
| | 672.35 | 0.0714 | 5.95 | iii, C-Si stretching | 1238.93 | 0.0495 | 7.60 | i, ii |
| | 722.62 | 0.0610 | 5.46 | iii, C-Si stretching | 2221.30 | 0.0276 | 7.59 | C≡C stretching |
| | 1434.27 | 0.0277 | 4.92 | i, ii, ix | 1434.27 | 0.0393 | 6.99 | i, ii, ix |
| | 1345.67 | 0.0189 | 3.15 | i, ii | 1432.56 | 0.0308 | 5.47 | i, ii, ix |
| | 1432.56 | 0.0167 | 2.97 | i, ii, ix | 1564.19 | 0.0258 | 5.00 | i, ii |
| | 1594.70 | 0.0138 | 2.74 | i, ii | 802.16 | 0.0459 | 4.56 | ii, iii |
| | 501.34 | 0.0371 | 2.30 | viii | 618.10 | 0.0479 | 3.67 | iii, viii |
| | 355.95 | 0.0460 | 2.03 | viii | 1345.67 | 0.0216 | 3.60 | i, ii |
| | 1194.71 | 0.0110 | 1.63 | i | 722.62 | 0.0333 | 2.99 | iii, C-Si stretching |
| | 417.81 | 0.0305 | 1.58 | viii | 1194.71 | 0.0201 | 2.97 | i |
| | 1056.72 | 0.0116 | 1.51 | ix | 501.34 | 0.0419 | 2.60 | viii |
| | 394.11 | 0.0301 | 1.47 | iii, viii | 355.95 | 0.0436 | 1.93 | viii |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 435.09 | 0.0199 | 1.07 | iii, viii | 1056.72 | 0.0126 | 1.66 | ix |
| 1122.92 | 0.0075 | 1.04 | i, ii | 435.09 | 0.0305 | 1.64 | iii, viii |
| | | | | 1122.92 | 0.0115 | 1.60 | i, ii |
| | | | | 394.11 | 0.0316 | 1.54 | iii, viii |
| | | | | 182.66 | 0.0652 | 1.48 | viii |
| | | | | 417.81 | 0.0235 | 1.22 | viii |

[a] Vibration types: (i) in-plane bending vibration of aromatic H (Ar–H); (ii) aromatic ring stretching vibration; (iii) aromatic ring in-plane bending vibration; (iv) C–N stretching vibration; (v) C=O stretching vibration; (vi) out-of-plane bending vibration of Ar-H; (vii) aromatic ring out-of-plane bending vibration; (viii) the rocking/wagging vibrations of $–CH_2–$ and $–CH_3$ in the side chain (namely, $–CH_2–$ or $–CH_3$ is vibrating as a whole); (ix) $–CH_2–$ or $–CH_3$ deformation vibration. The major contributed vibration type of each mode is underline.

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