Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Electronic Supplementary Information

## *Fluorescent Emissions of Imide Compounds and End-Capped Polyimides Enhanced by Intramolecular Double Hydrogen Bonds*

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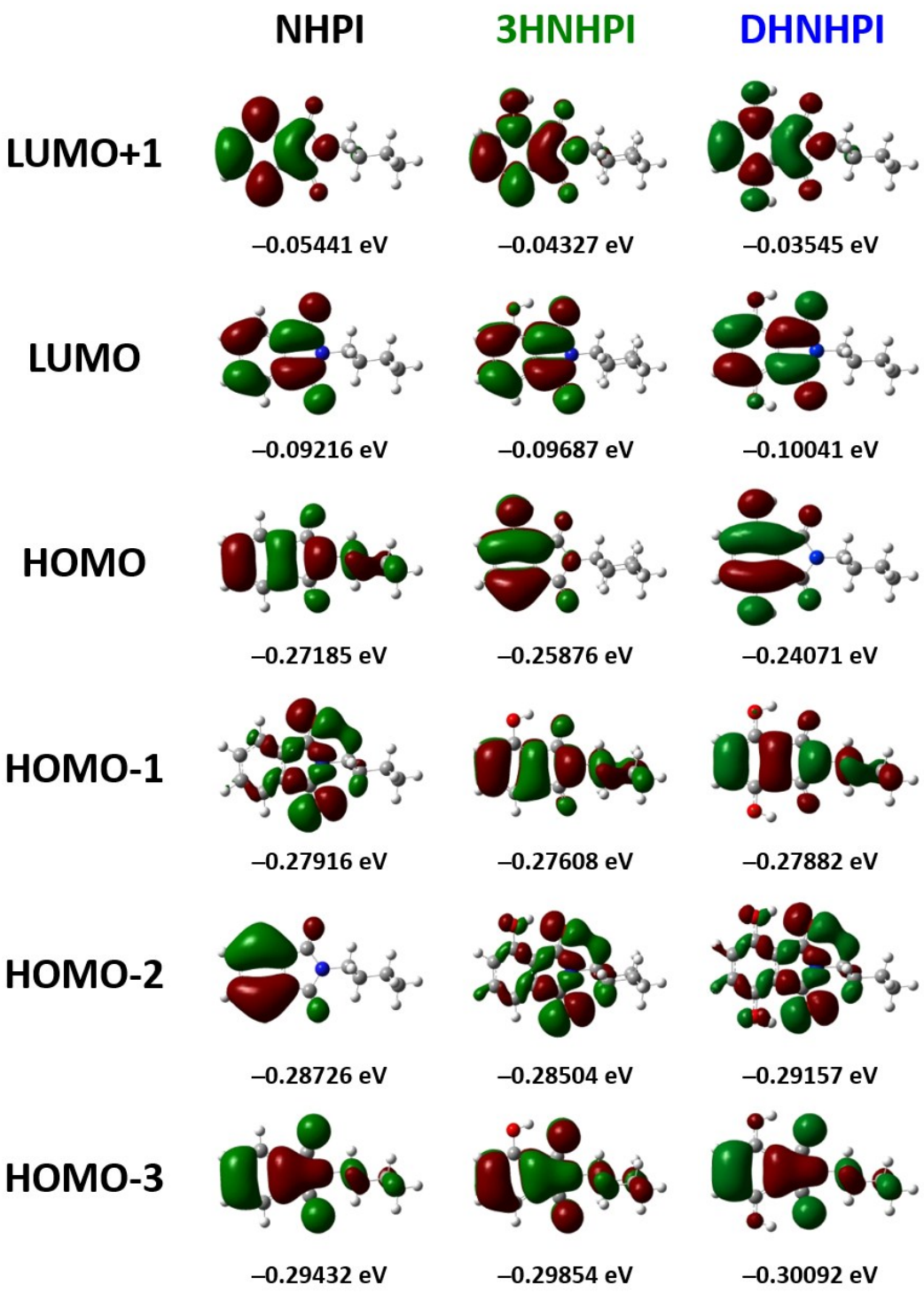



Fig. S1. Calculated MOs of NHPI, 3HNHPI, and DHNHPI (TD-DFT method at B3LYP/6-311++G(d,p) level). HOMO–*m* and LUMO+*m* denote (*m*+1)th highest occupied orbital and (*m*+1)th lowest unoccupied orbital.

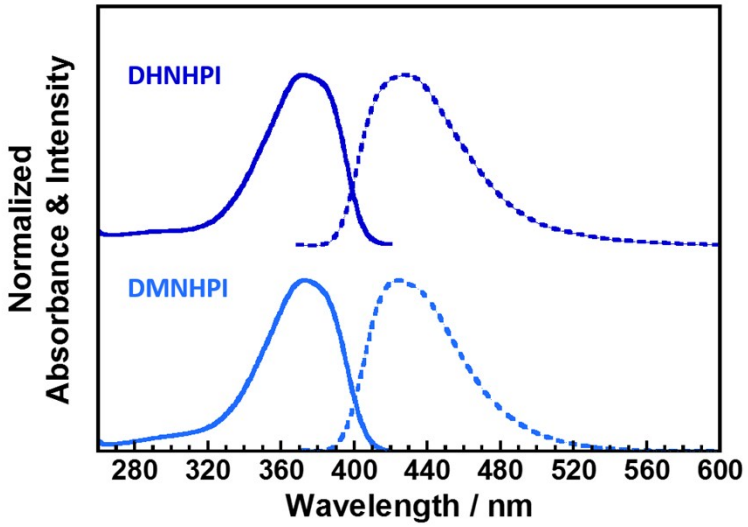



Fig. S2. UV-vis (solid line) and emission (broken line) spectra of DHNHPI and DMNHPI ($5 \times 10^{-5}$ M) in $CHCl_3$. Excitation wavelengths are 369 nm (DHNHPI) and 372 nm (DMNHPI).

| State | Transition wavelength / nm | Oscillator strength | Orbital | | | Assignment |
|---|---|---|---|---|---|---|
| $S_1$ | 469.5 | 0.1525 | HOMO | → | LUMO | $\pi$–$\pi$* |
| $S_2$ | 443.7 | 0.0000 | HOMO | → | LUMO+1 | $\pi$–$r$* |
| $S_3$ | 436.2 | 0.0000 | HOMO−1 | → | LUMO | $n$–$\pi$* |
| $S_4$ | 377.2 | 0.0001 | HOMO | → | LUMO+2 | $\pi$–$r$* |
| $S_5$ | 370.3 | 0.0006 | HOMO | → | LUMO+3 | $\pi$–$r$* |

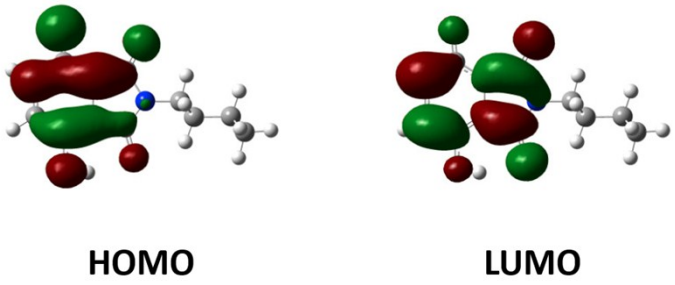



Fig. S3. Calculated electronic transitions of $DHNHPI^-$ in optimized $S_0$ geometry and spatial distributions of HOMO and LUMO (TD-DFT method at B3LYP/6-311++G(d,p) level).

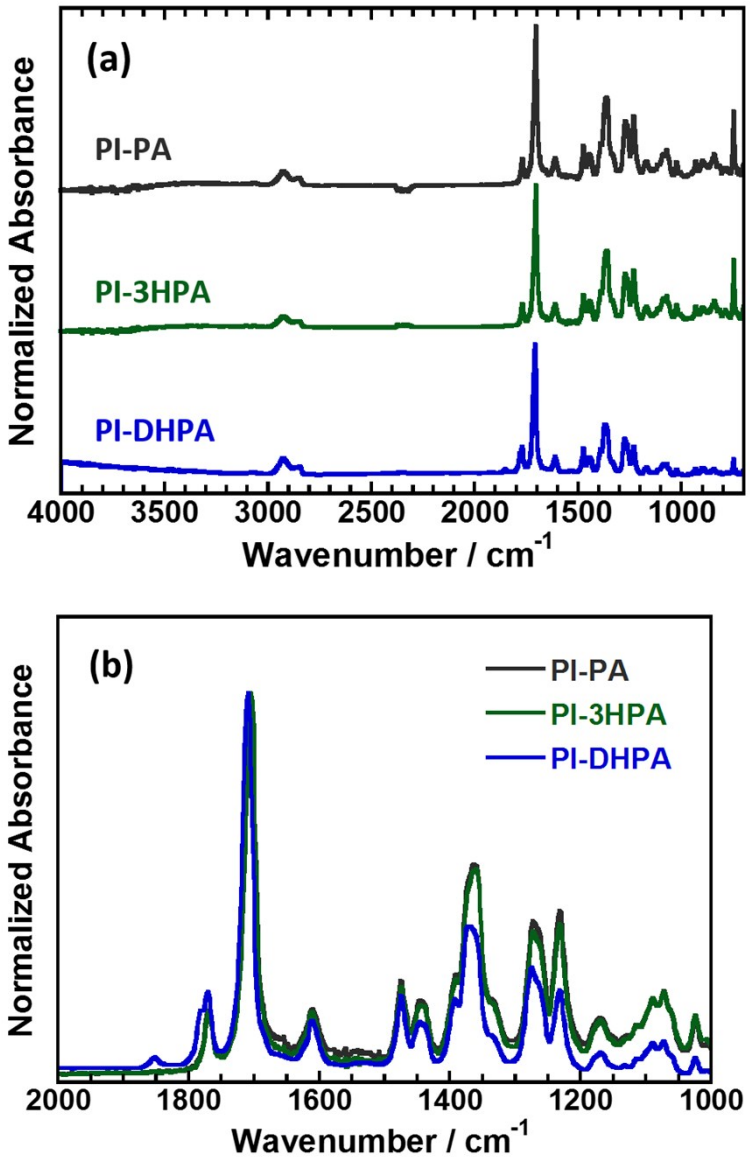



Fig. S4. Fourier transform ATR FT-IR spectra of PI-PA, PI-3HPA, and PI-DHPA films. Spectra are normalized at asymmetric C=O stretching bands. (a) Overall view and (b) enlarged view in range from 1000 $cm^{-1}$ to 2000 $cm^{-1}$.

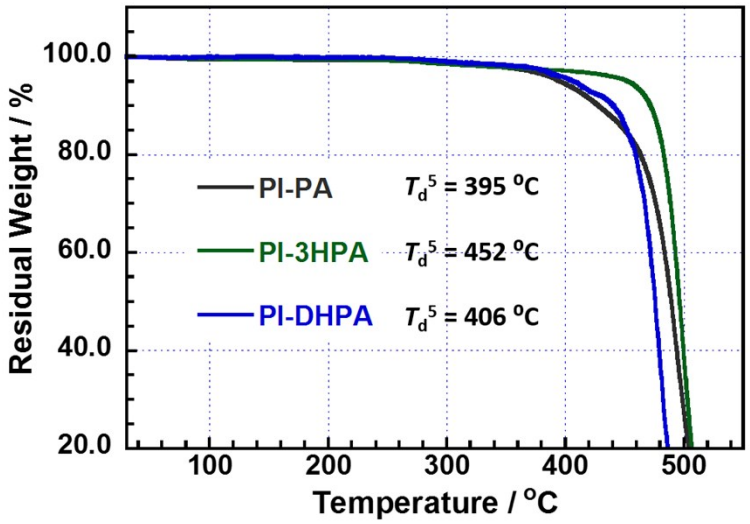



Fig. S5. TGA curves of PI-PA, PI-3HPA, and PI-DHPA films.

Table S1. Calculated Energies (E(RB3LYP)) of Isomers and Tautomers of DHNHPI in Optimized $S_0$ Geometry.

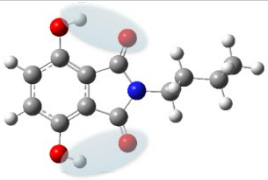
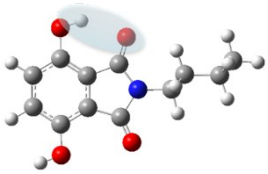
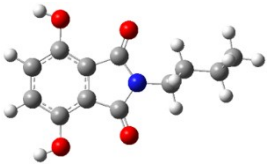
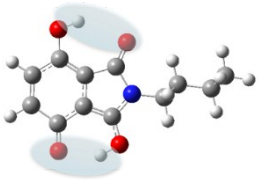
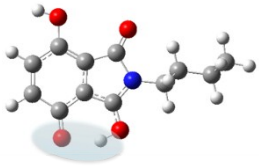
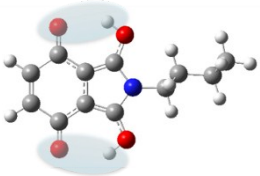
| | E(RB3LYP) / hartree | Energy difference from enol-cis form / kJ/mol |
|---|---|---|
|  **enol-cis** | –898.4367896 | 0.0 |
|  **enol-trans** | –898.4261562 | 27.9 |
|  **ditrans** | –898.4123679 | 64.1 |
|  **keto-cis** | –898.4032674 | 88.0 |
|  **keto-trans** | –898.3941411 | 112.0 |
|  **diketo** | –898.3847372 | 136.7 |

Table S2. Crystal Data and Experimental Details of 3HNHPI and DHNHPI.

| | **3HNHPI** | **DHNHPI** |
|---|---|---|
| Chemical formula | $C_{14}H_{15}NO_3$ | $C_{14}H_{15}NO_4$ |
| Fomula weight | 245.27 | 261.27 |
| Temp [K] | 173(2) | 173(2) |
| Wavelength [Å] | 1.54186 | 1.54186 |
| Cryst syst | Orthorhombic | Triclinic |
| Space group | *C m c* $2_1$ | *P* –1 |
| *a* [Å] | 6.6923(2) | 5.09090(10) |
| *b* [Å] | 7.5956(2) | 5.20710(10) |
| *c* [Å] | 22.7742(6) | 23.0054(4) |
| Vol [Å$^3$] | 1157.66(6) | 599.675(19) |
| Z | 4 | 2 |
| Calcd density [Mg m$^{-3}$] | 1.407 | 1.447 |
| Abs coeff [mm$^{-1}$] | 0.813 | 0.886 |
| F(000) | 520 | 276 |
| Cryst size [mm$^3$] | 0.24 × 0.10 × 0.07 | 0.23 × 0.21 × 0.02 |
| $\theta$ range for data collection | 3.88° to 68.00° | 3.87° to 68.22° |
| Index ranges | –8<=h<=8, –9<=k<=9, –27<=l<=27 | –5<=h<=5, –6<=k<=6, –27<=l<=27 |
| Reflns collected | 6308 | 7110 |
| Indep reflns | 590 [$R_{int}$ = 0.0639] | 2142 [$R_{int}$ = 0.0393] |
| completeness to $\theta$ | 100.00% | 97.90% |
| abs correction | semi-empirical from equivalents | semi-empirical from equivalents |
| Max and min transm | 0.9453 and 0.6266 | 0.9790 and 0.6529 |
| Refinement meth | Full-matrix least-squares on F$^2$ | Full-matrix least-squares on F$^2$ |
| Data / Restrains / Params | 590 / 1 / 103 | 2142 / 0 / 232 |
| Goodness-of-fit on F$^2$ | 1.113 | 1.212 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1$ = 0.0342, $wR_2$ = 0.0892 | $R_1$ = 0.0430, $wR_2$ = 0.1339 |
| *R* indices (all data) | $R_1$ = 0.0371, $wR_2$ = 0.0933 | $R_1$ = 0.0510, $wR_2$ = 0.1390 |
| Largest diff peak, hole [e·Å$^{-3}$] | 0.180 and –0.209 | 0.316 and –0.187 |

Table S3. Representative Bond Lengths, Bond Angles, and Dihedrals Angles of 3HNHPI and DHNHPI in Single-Crystal.

| | **3HNHPI** | **DHNHPI** | |
|---|---|---|---|
| Length / Å | | A | B |
| H1–O2 | 0.841(3) | 0.92(4) | 0.88(4) |
| O2–C3 | 1.345(5) | 1.365(3) | 1.353(3) |
| C3–C4 | 1.382(5) | 1.371(3) | 1.386(3) |
| C4–C5 | 1.477(5) | 1.465(3) | – |
| C7–C8 | 1.498(5) | 1.484(3) | – |
| C5–O6 | 1.220(4) | 1.224(3) | – |
| C8–O9 | 1.215(5) | 1.214(3) | – |
| H1–O6 | 2.354(3) | 2.17(4) | 2.64(3) |
| O2–O6 | 3.039(4) | 2.938(2) | 3.245(2) |
| C4–C7 | 1.386(5) | 1.397(3) | – |
| C5–N10 | 1.395(4) | 1.387(3) | – |
| C8–N10 | 1.397(5) | 1.408(3) | – |
| Angle / deg. | | | |
| O2H1C3 | 109.5(3) | 109(2) | 116(2) |
| O2C3C4 | 124.9(4) | 123.0(2) | 126.2(2) |
| O2H1O6 | 139.0(2) | 140(3) | 127(3) |
| C5O6H1 | 90.9(2) | 94(1) | 89.0(8) |
| Dihedral / deg. | | | |
| H1O2C3C4 | –0.0(5) | –2(2) | –1(3) |
| O6H1O2C3 | –0.0(5) | 3(5) | 1(4) |
| C5O6H1O2 | –0.0(4) | –3(5) | –1(3) |
| C3C4C5O6 | –0.0(6) | 0.7(4) | – |
| O2C3C4C5 | 0.0(7) | –0.0(3) | 1.8(4) |