Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


# Multistimuli and fingertip-triggered luminescence switching: Five colored ink-free rewritable secured platform with strongest red emission

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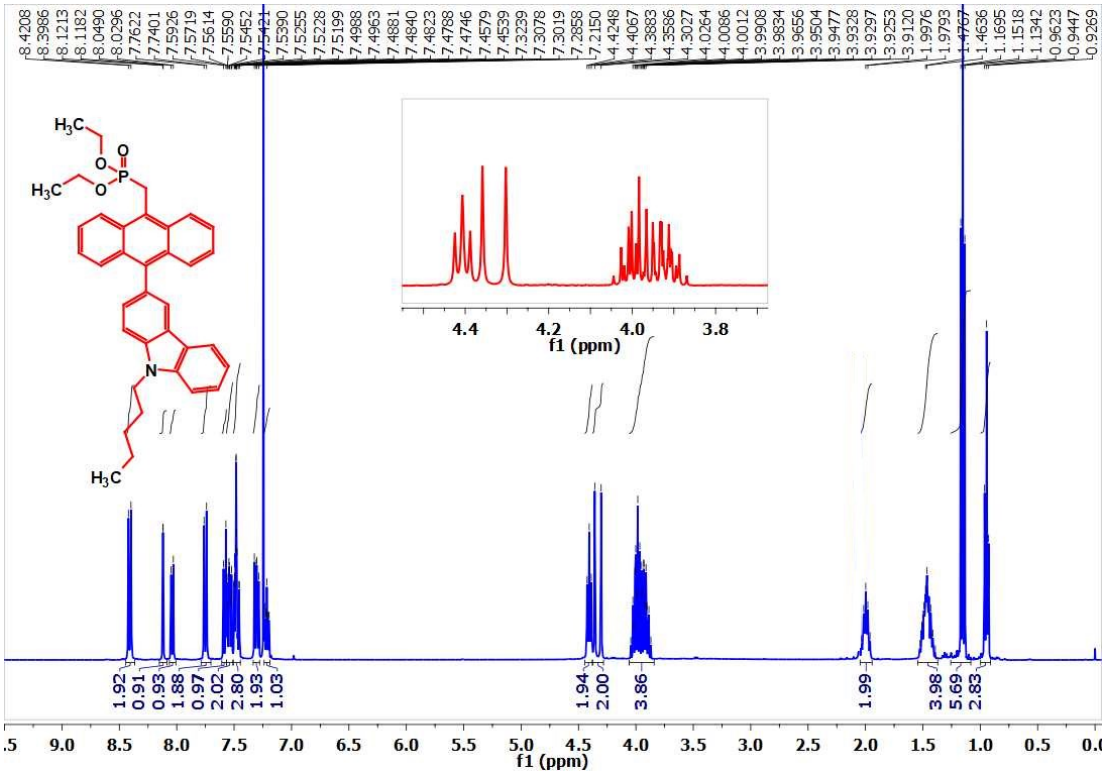



**Fig S1:** $^{1}$H NMR spectrum for **C5CBZP** in $CDCl_3$.

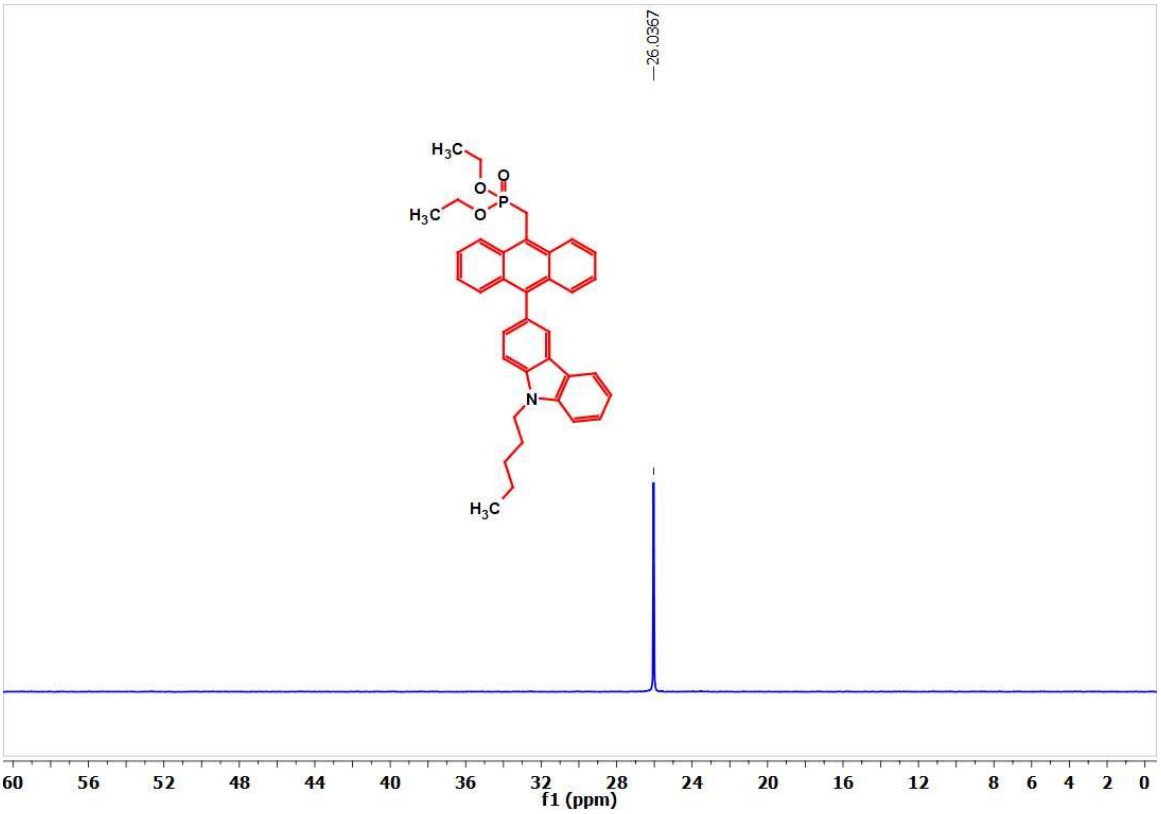



**Fig S2:** $^{31}P$ NMR spectrum for **C5CBZP** in $CDCl_3$.

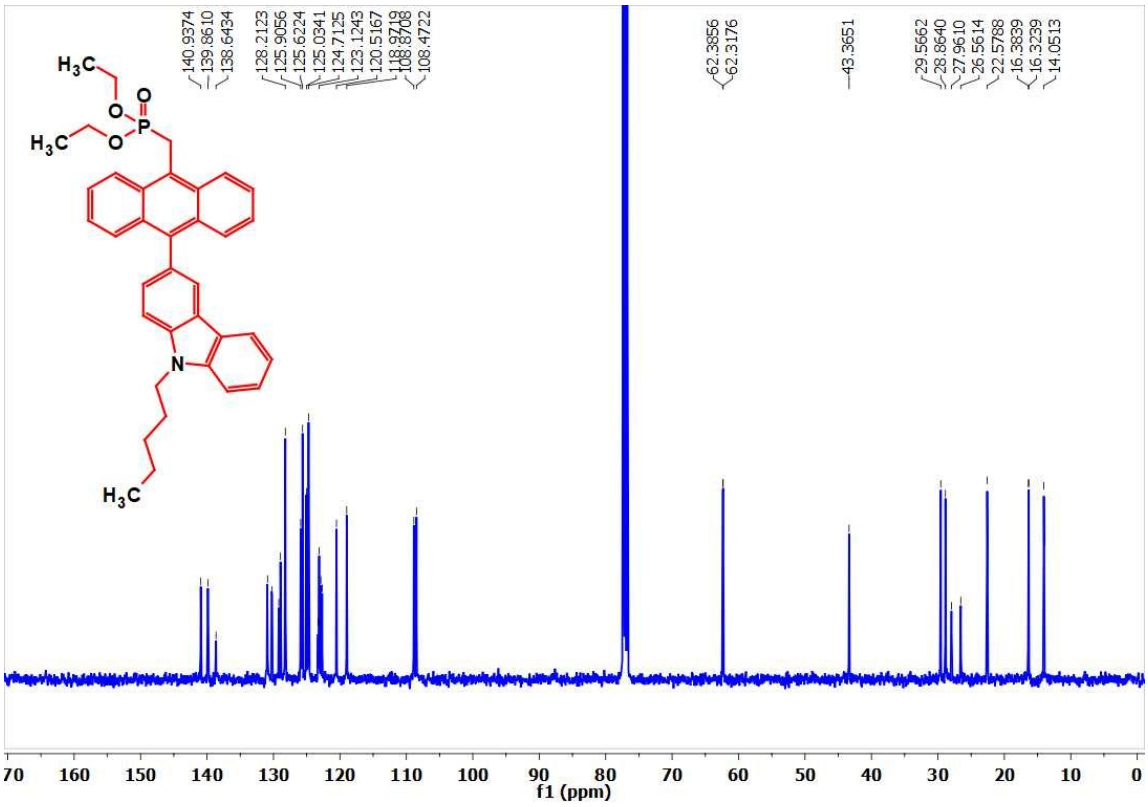



**Fig S3:** $^{13}C$ NMR spectrum for **C5CBZP** in $CDCl_3$.

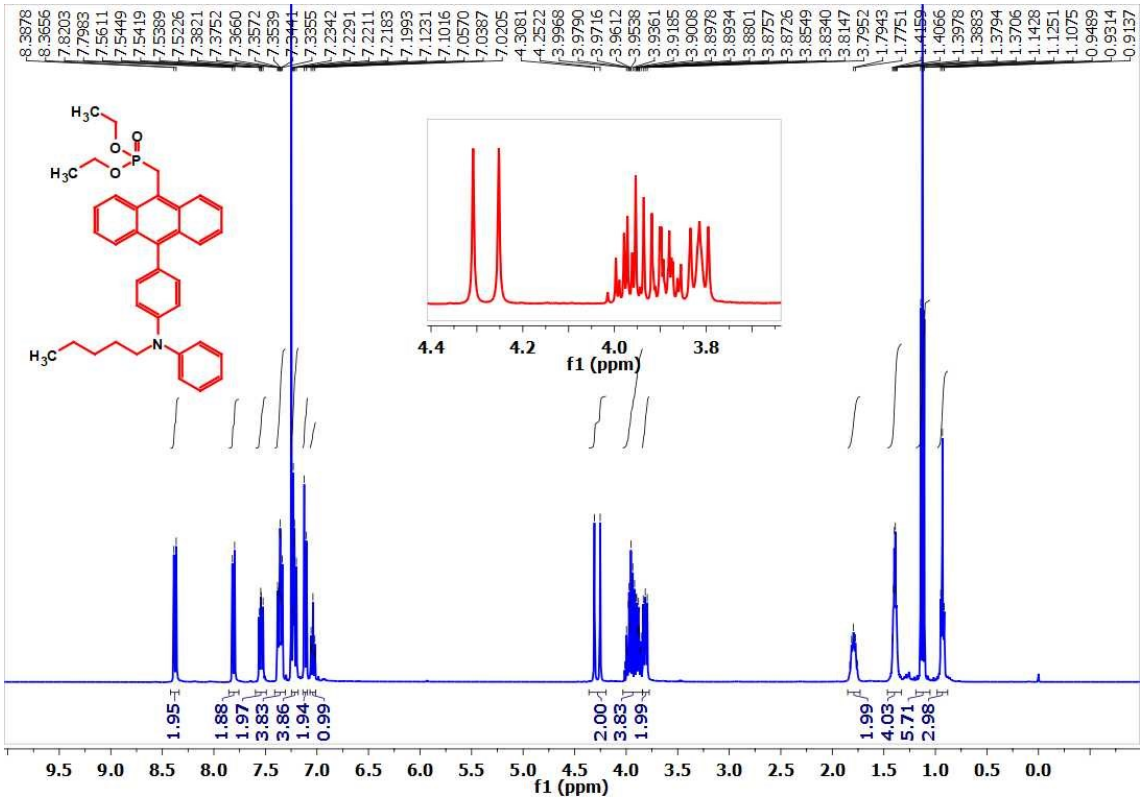



**Fig S4:** $^{1}$H NMR spectrum for **C5DPAP** in $CDCl_3$.

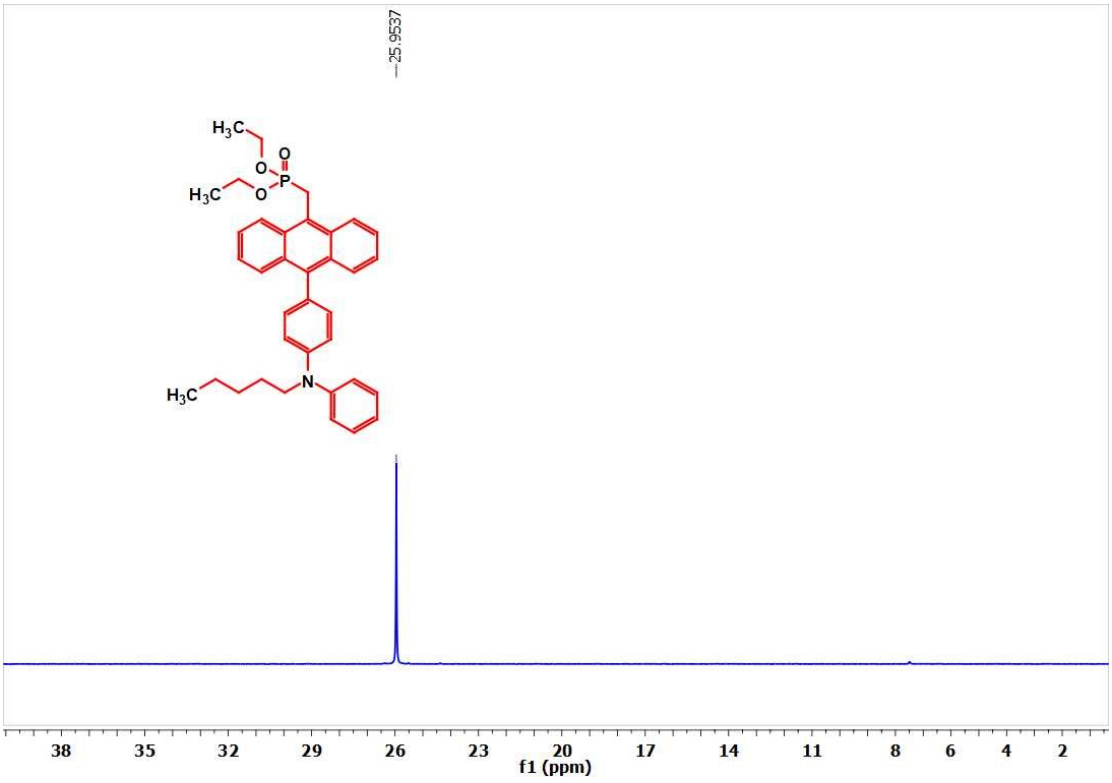



**Fig S5:** $^{31}$P NMR spectrum for **C5DPAP** in $CDCl_3$.

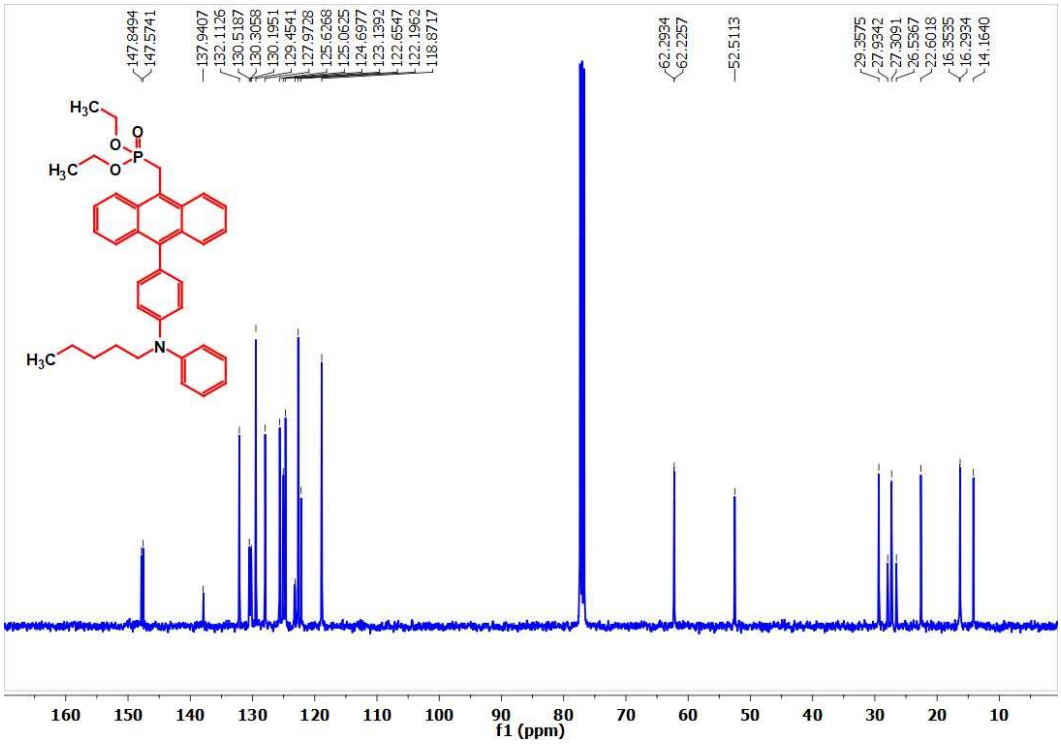



**Fig S6:** $^{13}C$ NMR spectrum for **C5DPAP** in $CDCl_3$.

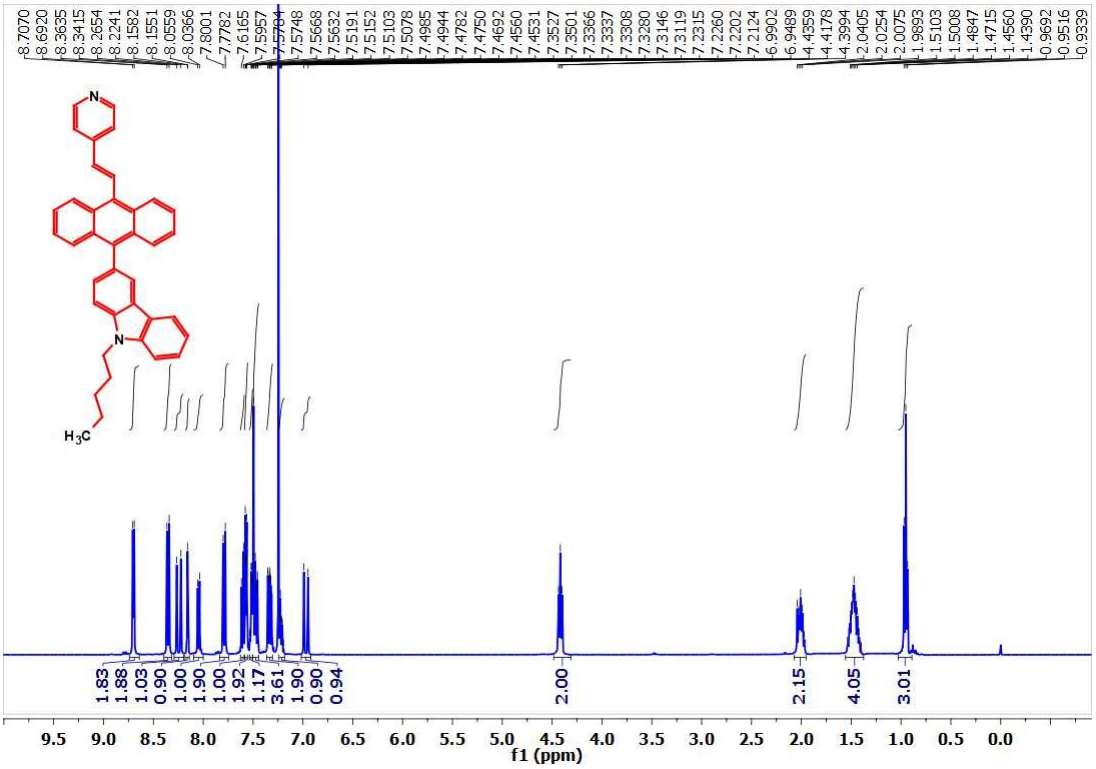



**Fig S7:** $^{1}H$ NMR spectrum for **CBZ4Py** in $CDCl_3$.

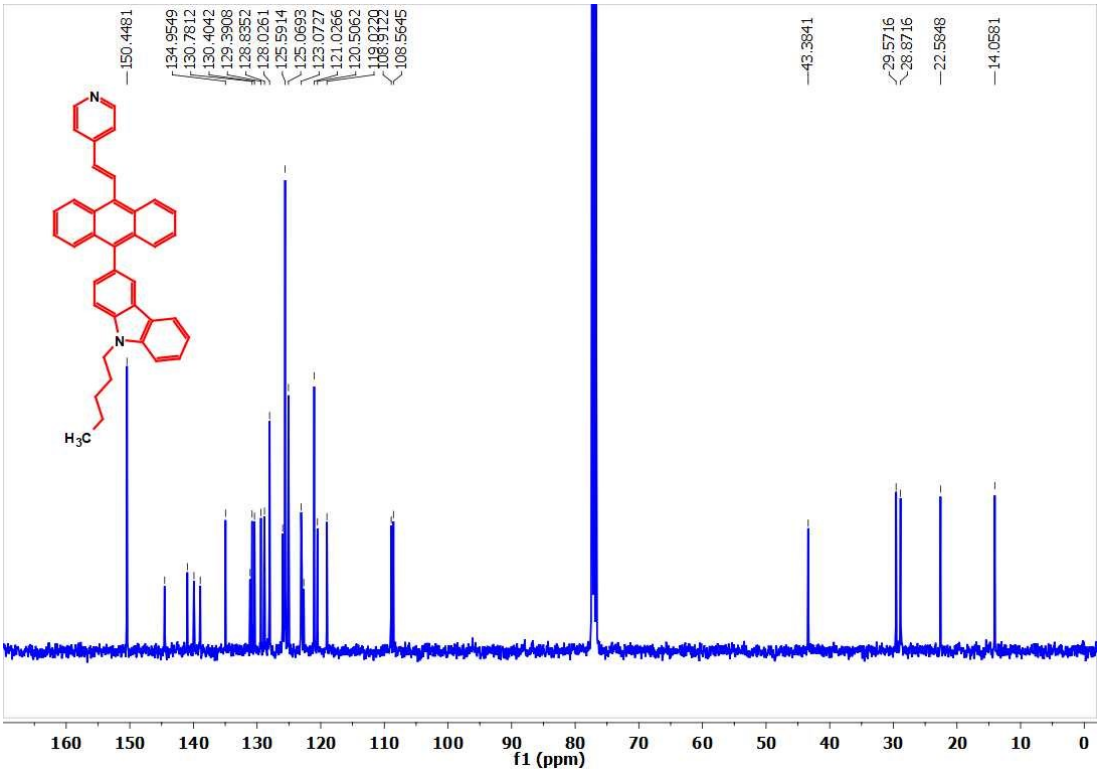



**Fig S8:** $^{13}C$ NMR spectrum for **CBZ4Py** in $CDCl_3$.

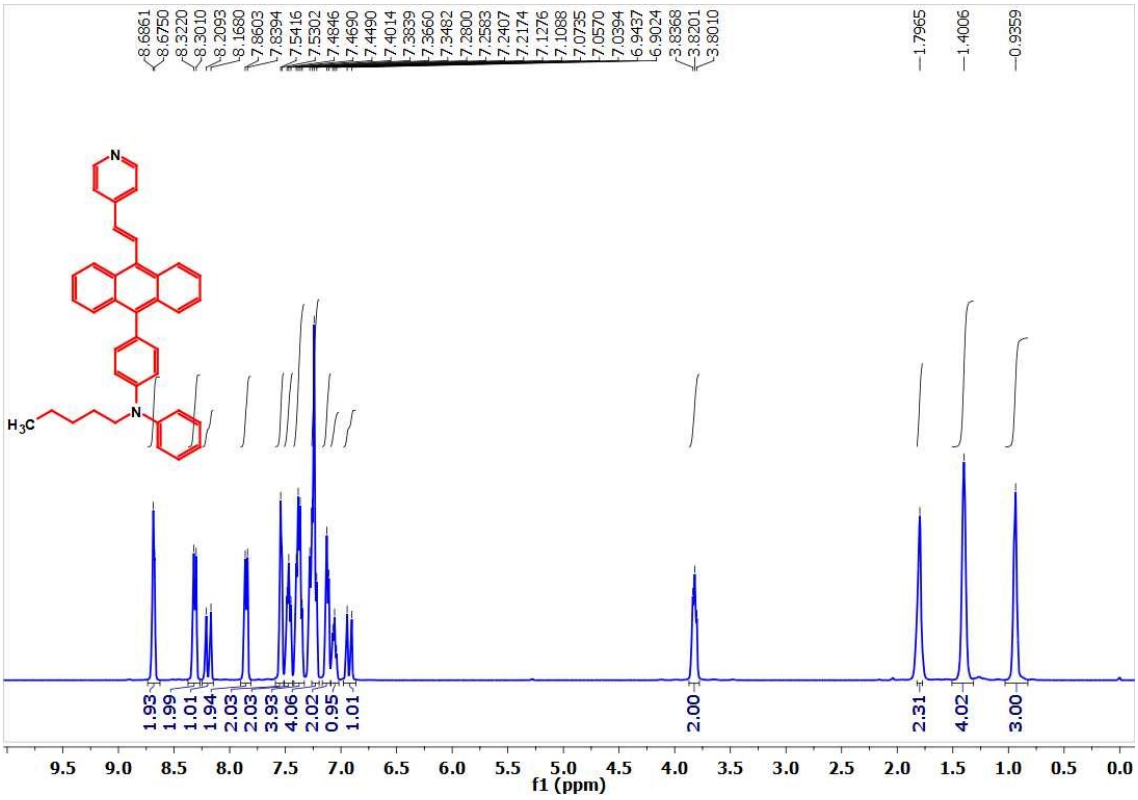



**Fig S9:** $^{1}H$ NMR spectrum for **DPA4Py** in $CDCl_3$.

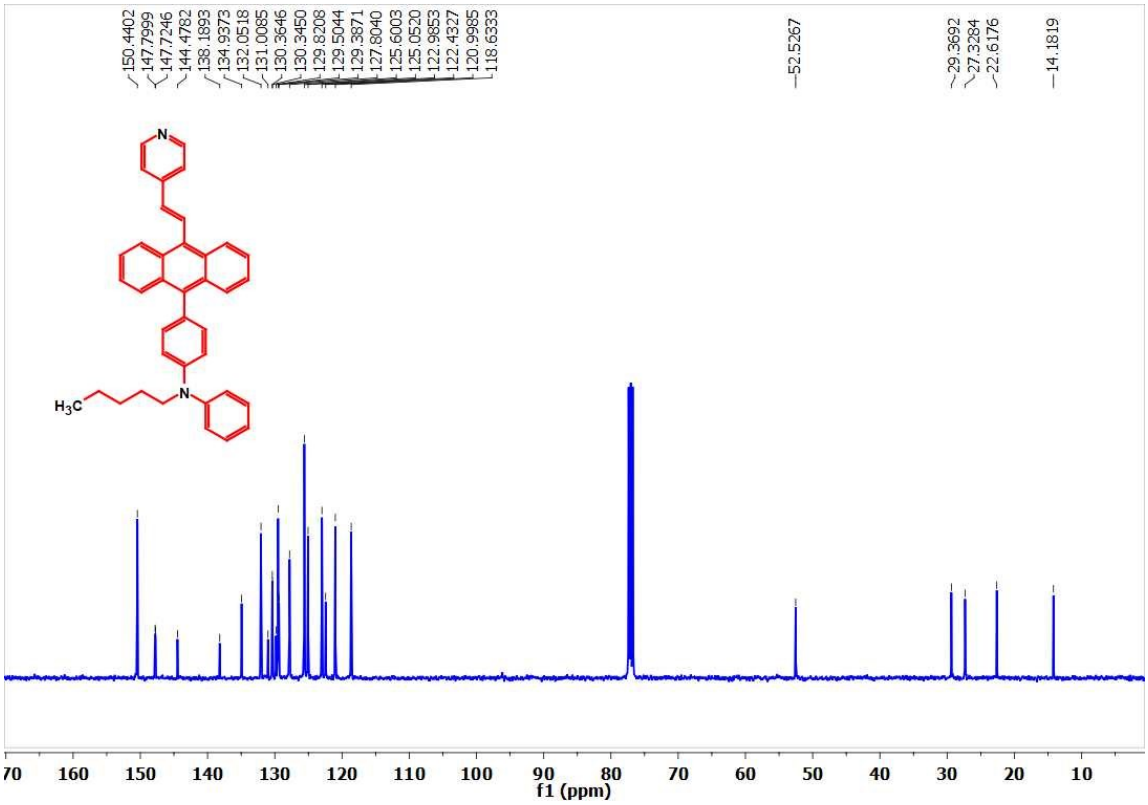



**Fig S10:** $^{13}C$ NMR spectrum for **DPA4Py** in $CDCl_3$.

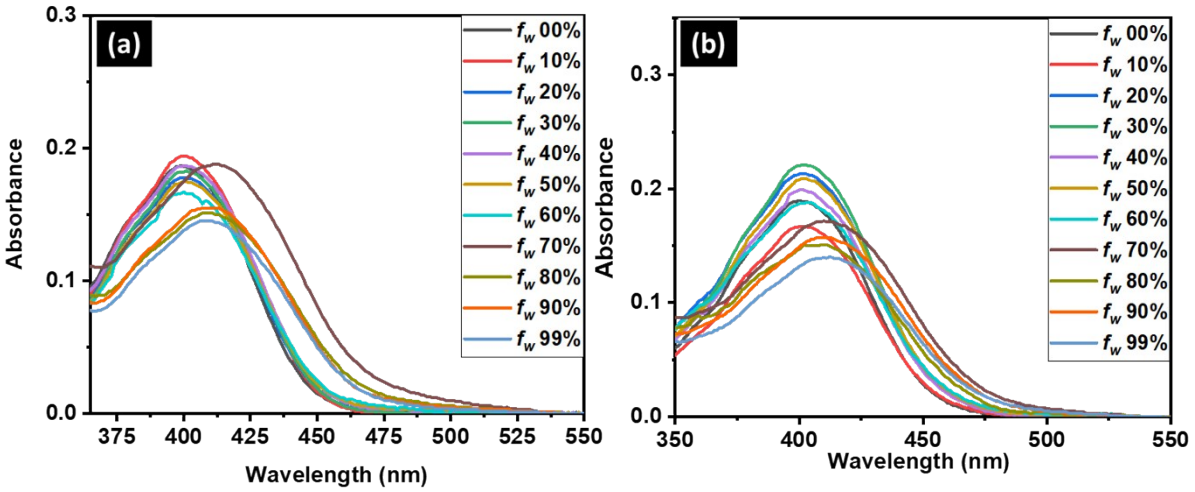



**Fig S11:** Absorbance spectra with different fractions of water in MeCN for (a) **CBZ4Py** and (b) **DPA4Py.** (10 μM).

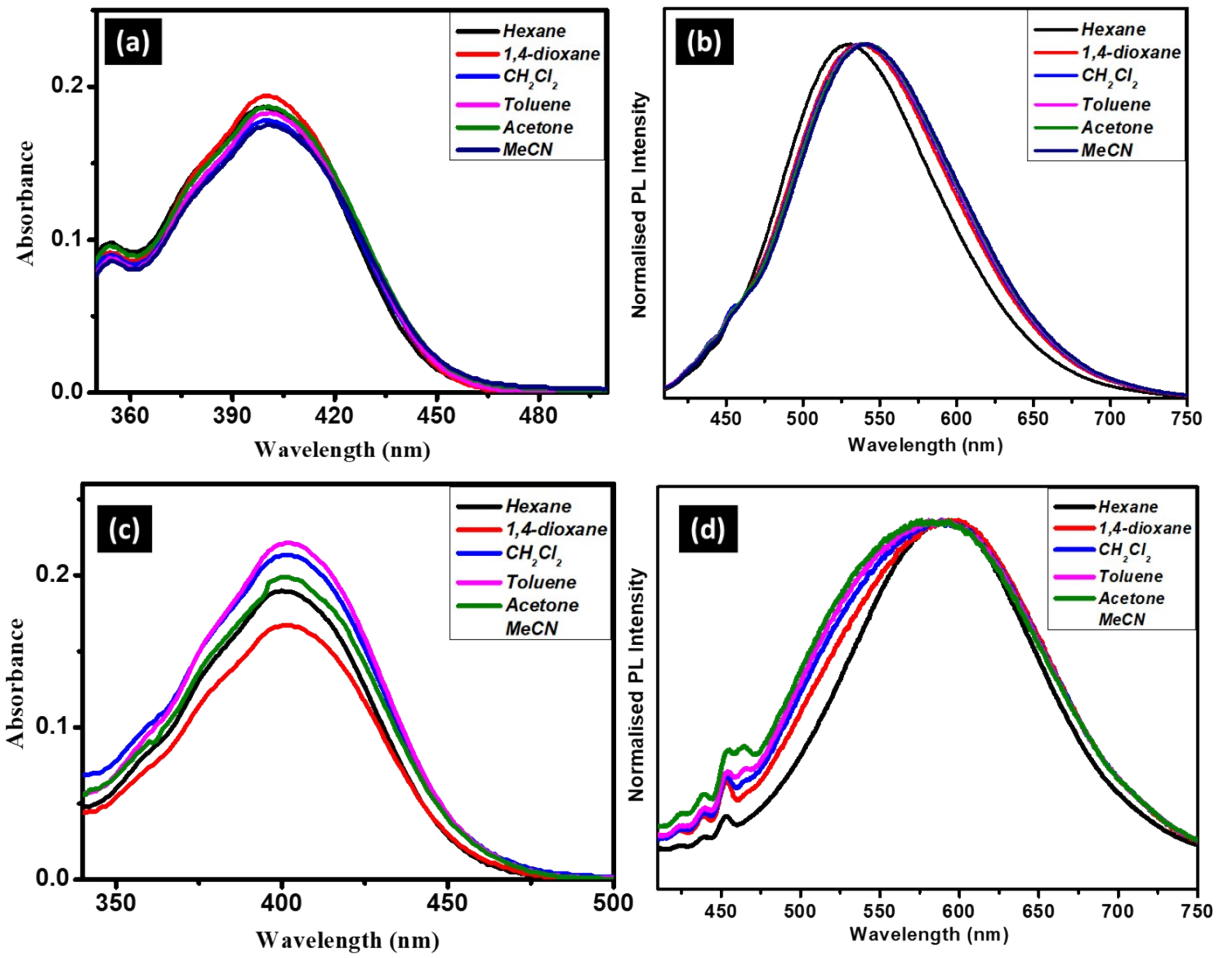



**Fig S12:** (a) Absorbance spectra in different solvent for (a) **CBZ4Py**, (c) **DPA4Py** and PL spectra in different solvents for (b) **CBZ4Py**, (d) **DPA4Py**.

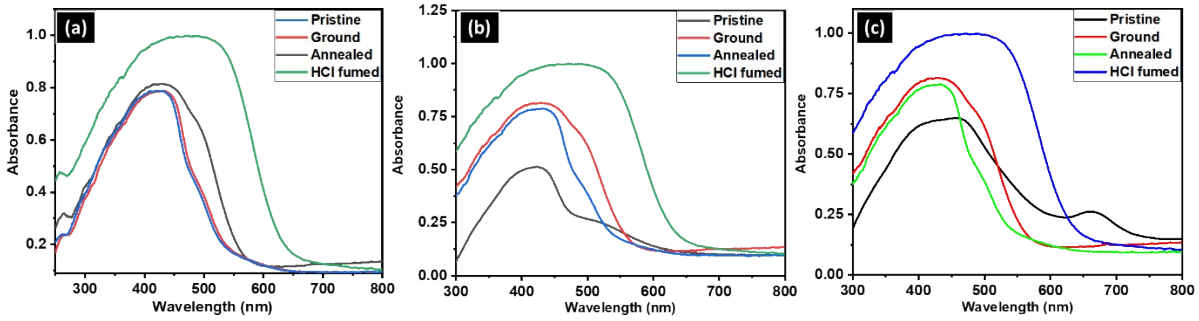



**Fig S13:** Absorbance spectra with different stimuli for (a) **CBZ4Py** and (b) **DPA4Py-B**, (c) **DPA4Py-G.**

**Table-S1**: Crystallographic parameters for **CBZ4Py**, **DPA4Py-B** and **DPA4Py-G**

| **Compounds** | **CBZ4Py** | **DPA4Py-B** | **DPA4Py-G** |
|---|---|---|---|
| Emp. Formula | C38 H32 N2 | C38 H34 N2 | C38 H34 N2 |
| Formula weight | 516.65 | 518.71 | 518.71 |
| Crystal system | monoclinic | orthorhombic | monoclinic |
| Space group | P 1 21/c 1 | P c a 21 | P 1 21/c 1 |
| *a* /Å | 13.6626(4) | 9.9341(2) | 18.7495(2) |
| *b* /Å | 9.4221(2) | 17.0176(4) | 9.09830(10) |
| *c* /Å | 21.1928(6) | 17.0876(3) | 18.4595(2) |
| /degree | 90 | 90 | 90 |
| /degree | 92.901(3) | 90 | 114.7790(10) |
| /degree | 90 | 90 | 90 |
| $V$ /Å$^3$ | 2724.66(13) | 2888.74(10) | 2859.06(6) |
| $Z$ | 4 | 8 | 4 |
| $D_{calc}$ /g cm$^{-3}$] | 1.260 | 1.193 | 1.205 |
| /mm$^{-1}$ | 0.555 | 0.524 | 0.529 |
| $F$ (000) | 1096.0 | 1104.0 | 1104.0 |
| Data/ restraints/ parameters | 5759 /0/359 | 4269/1/362 | 6084/0/362 |
| S | 1.059 | 1.053 | 1.031 |
| R1 [I>2(I)] | 0.0588 | 0.0520 | 0.0391 |
| wR2 [all data] | 0.1672 | 0.1434 | 0.1076 |
| Max./min. residual electron dens. [eÅ$^{-3}$] | 0.564/-0.333 | 0.0494/-0.2848 | 0.1936/-0.2230 |

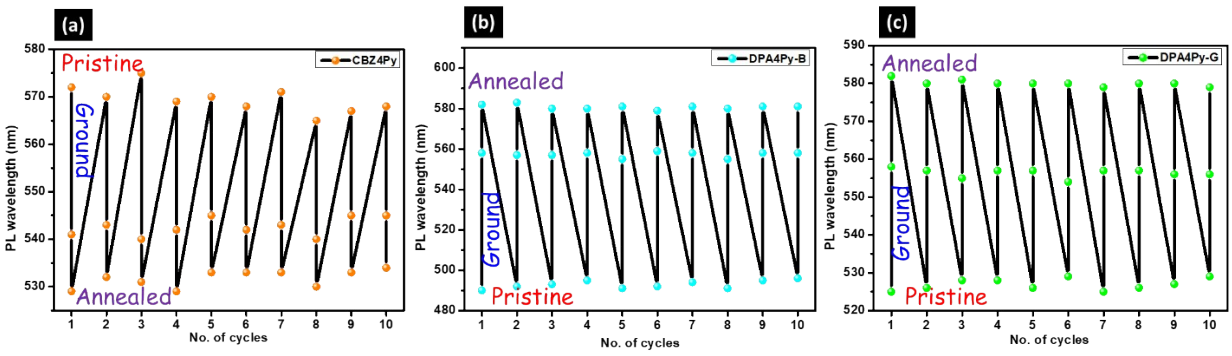



**Fig S14:** Reversibility towards external stimuli for **CBZ4Py**, **DPA4Py-B** and **DPA4Py-G**

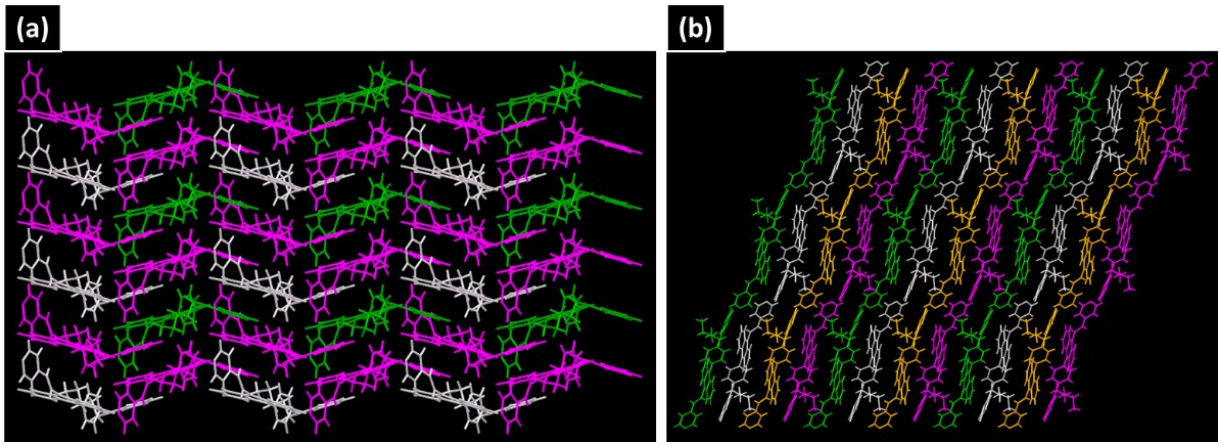



**Fig S15:** symmetry equivalence crystal packing for (a) **DPA4Py-B**, (b) **DPA4Py-G** along b-axis.

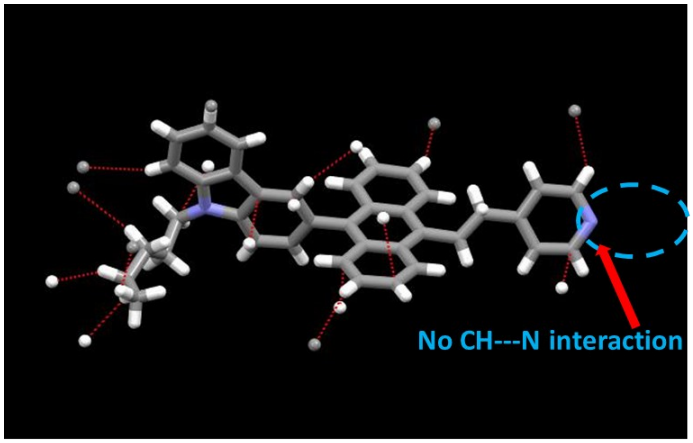



**Fig S16.** All probable intermolecular interactions for **CBZ4Py** (showing no CH---N interaction)

*Computational details*:

Geometry optimizations of all the compounds are carried out with the aid of Density functional theory (DFT) using Gaussian 16[1] suite of programs. B3LYP-D3[2-3] exchange-correlation functional along with 6-31G(d,p) basis set is used for all atoms. Further details are given in the supporting. Optimized geometries are further subjected to vibrational analysis to identify the structures as minima with all positive frequencies. Excited states calculations are performed using time-dependent density functional theory (TD-DFT) methods with long-range corrected CAM-B3LYP[4] exchange correlational functional in combination with 6-31+g(d,p) basis set.Gradient density plot calculations are carried out using Multiwfn 3.6 package.[5]

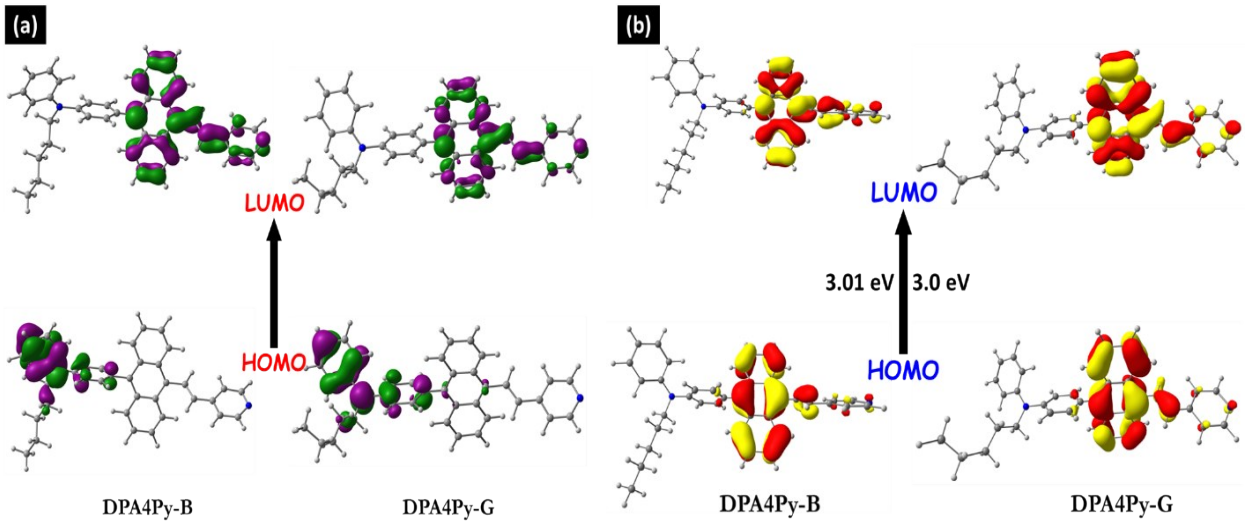



**Fig S17:** (a) Frontier molecular orbitals for **DPA4Py-B** (left) and **DPA4Py-G** (right), (b) NTO orbitals for optically excited states for **DPA4Py-B** (left) and **DPA4Py-G** (right)

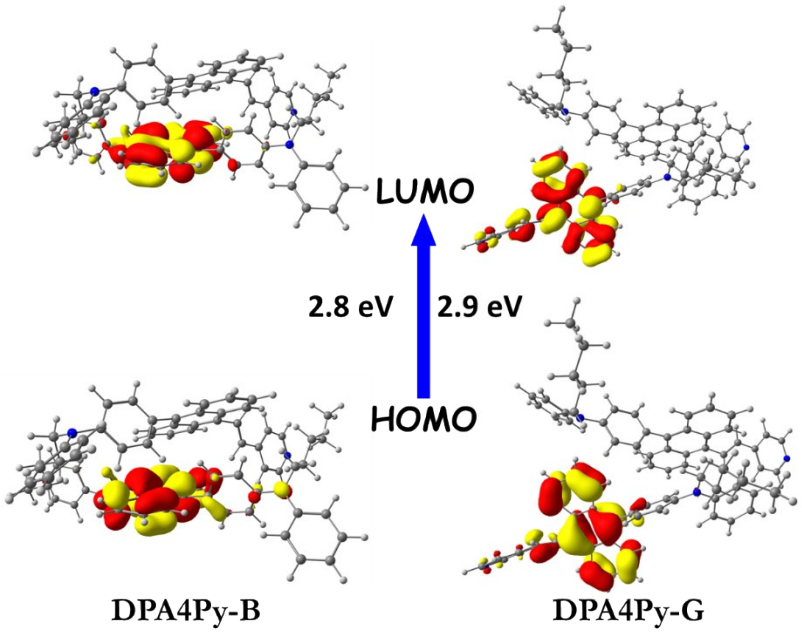



**Fig S18:** Optically excited states for **DPA4Py-B** and **DPA4Py-G** in dimeric form.

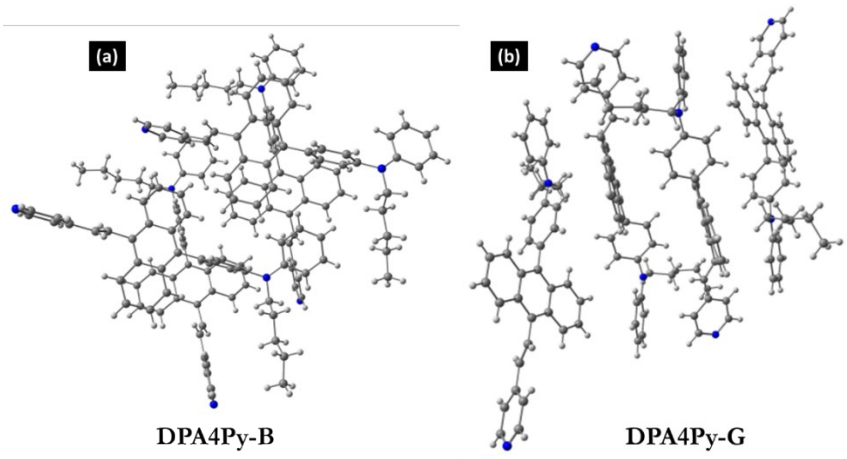



**Fig S19:** Optimized geometry in the tetrameric unit for (a) **DPA4Py-B** and (b) **DPA4Py-G**

***Hirshfeld Calculation:*** Hirshfeld surface analysis and calculation of the void space are quantitative tools used to understand non-covalent interactions. We have generated Hirshfeld surfaces for **DPA4Py-B** and **DPA4Py-G** with an isovalue of 0.5 au. The surface is generated, and the interactions are shown in terms of de and di, in which de and di are the distances of an atom external or internal to the generated Hirshfeld surfaces, together this pair (de and di) generates a 2D fingerprint plot. The different colors on the fingerprint plot represent the

frequency of occurrence of the interaction. A red spot represents the direct interaction between two atoms. Ultimately it gives a normalized contact distance (dnorm). The dnorm values are mapped onto the Hirshfeld surface using a red, white, and blue color scheme; red, white, and blue regions correspond to the strong, medium, and weak interactions, respectively. All the Hirshfeld surfaces were generated using Crystal Explorer 3.1 software. The void spaces were calculated with the iso value of 0.002 a.u. within a radius of the unit cell +5 Å (default).

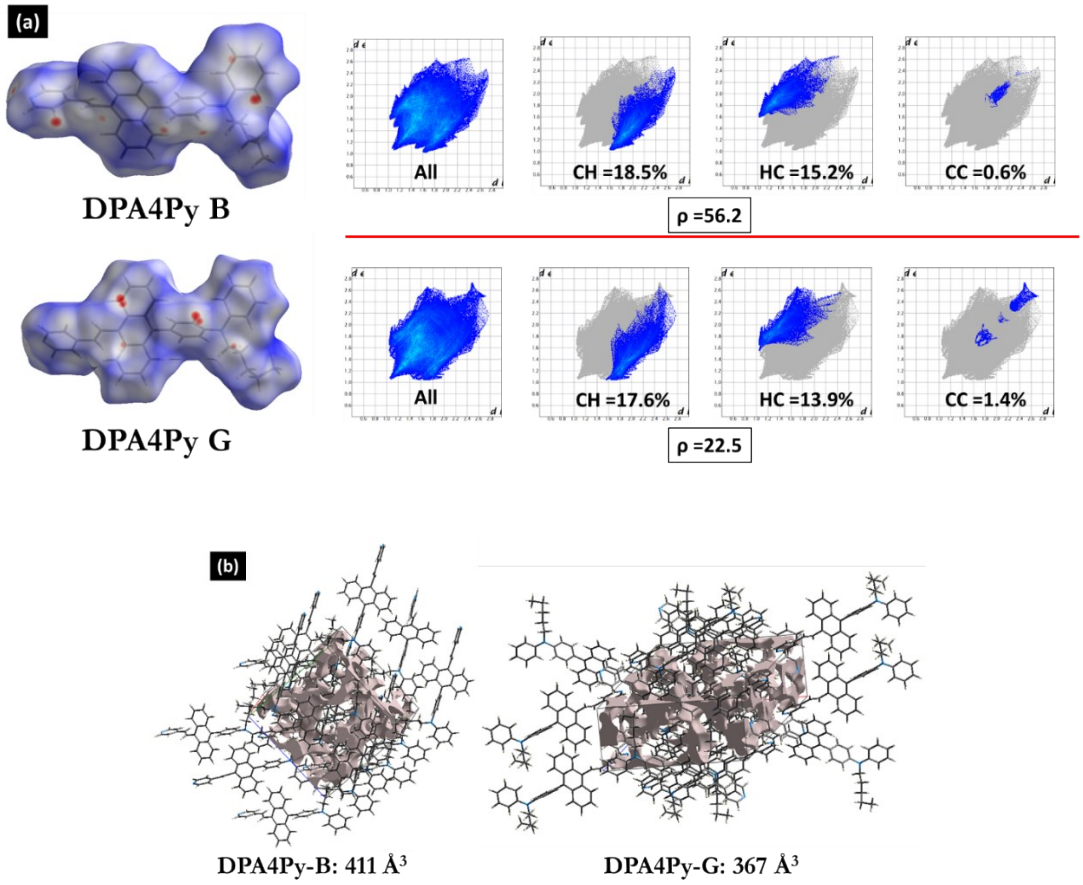
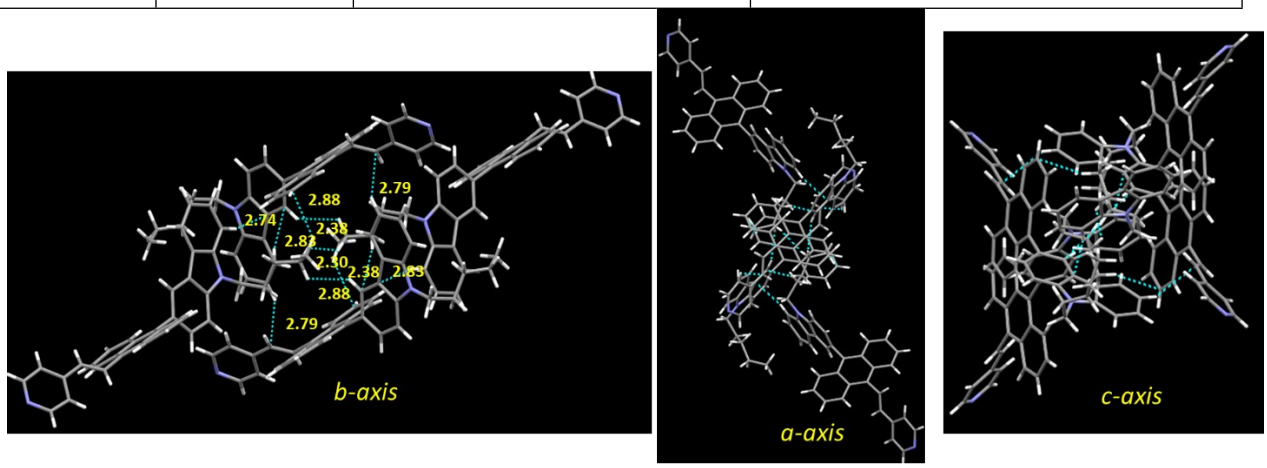



**Fig S20** (a) Hirshfeld surface mapped 2D fingerprint plots for **DPA4Py-B** and **DPA4Py-G,** (b) Hirshfeld generated unit cell void space for **DPA4Py-B** and **DPA4Py-G.**

**Table-S2**: All intermolecular interactions in molecular crystal packing for **CBZ4Py**, **DPA4Py-B** and **DPA4Py-G**

| Interactions | **CBZ4Py** | **DPA4Py-B** | **DPA4Py-G** |
|---|---|---|---|

| | | | |
|---|---|---|---|
| C---H | 2.85<br>2.88<br>2.74<br>2.83<br>2.88<br>2.79<br>2.87 | 2.88<br>2.75<br>2.88<br>2.85<br>2.84<br>2.82 | 2.81 (not CH…π)<br>2.80<br>2.79<br>2.88 (not CH…π)<br>2.88 |
| H---H | 2.30<br>2.37 | 2.36 | 2.38 |
| C---C | | 3.3 | 3.32<br>3.39 |
| N---H | | 2.65 | 2.72<br>2.68 |




These are the packing diagram with intermolecular interactions for **CBZ4Py**. Distances are in Å.

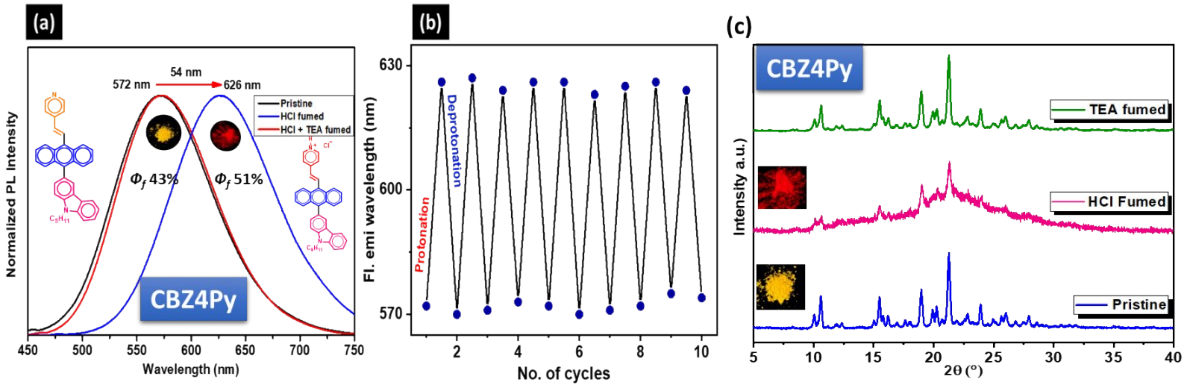



**Fig S21**: (a) Protonation/deprotonation PL spectra (b) PL reversibility cycles upon acidification (c) Change in PXRD pattern after protonation for **CBZ4Py**

**Table S3:** PL behaviour of **CBZ4Py** towards different acids

| Acids | $\lambda_{emi}$ (nm) | $\Phi_f$ (%, absolute) * |
|---|---|---|
| Hydrochloric acid (HCl | 626 | 51 |
| Trifluoroacetic acid (TFA) | 624 | 49.5 |
| Trifluoromethanesulfonic acid (TfOH) | 625 | 50.5 |
| Sulfuric acid ($H_2SO_4$)# | 626 | 58.5 |

* The absolute quantum yield was measured using a calibrated integrating sphere having an absolute error of ±2%

#We have generated the fumes by heating (using hot air gun) concentrated $H_2SO_4$ taken in a small glass vial. The fume was taken through a silicone pipe and linked to the vial containing the probe. The acidification experiment was performed inside an effective fume hood.

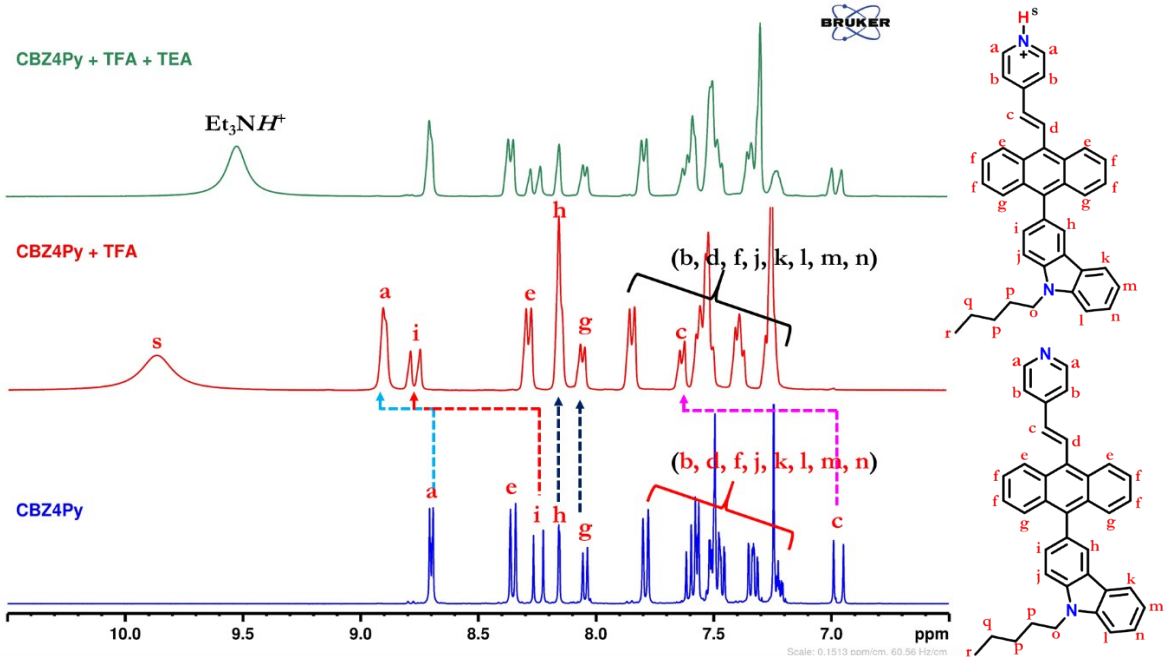



**Fig S21**: $^1$H NMR titration with TFA/TEA for **CBZ4Py** in $CDCl_3$ (for aromatic protons)

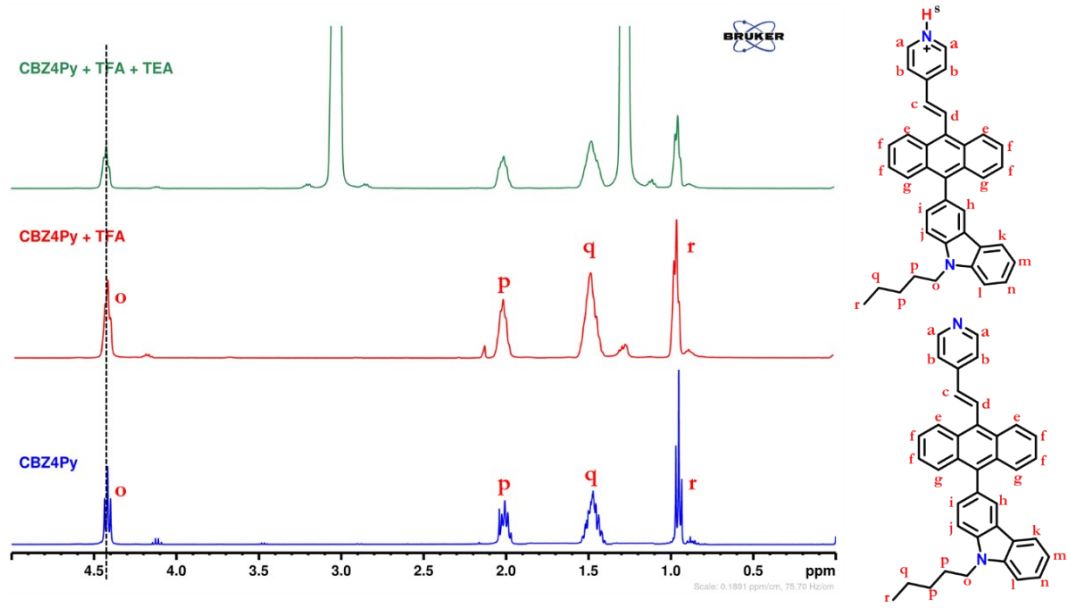



**Fig S22**: $^{1}$H NMR titration with TFA/TEA for **CBZ4Py** in $CDCl_3$ (for aliphatic protons without any shifts)

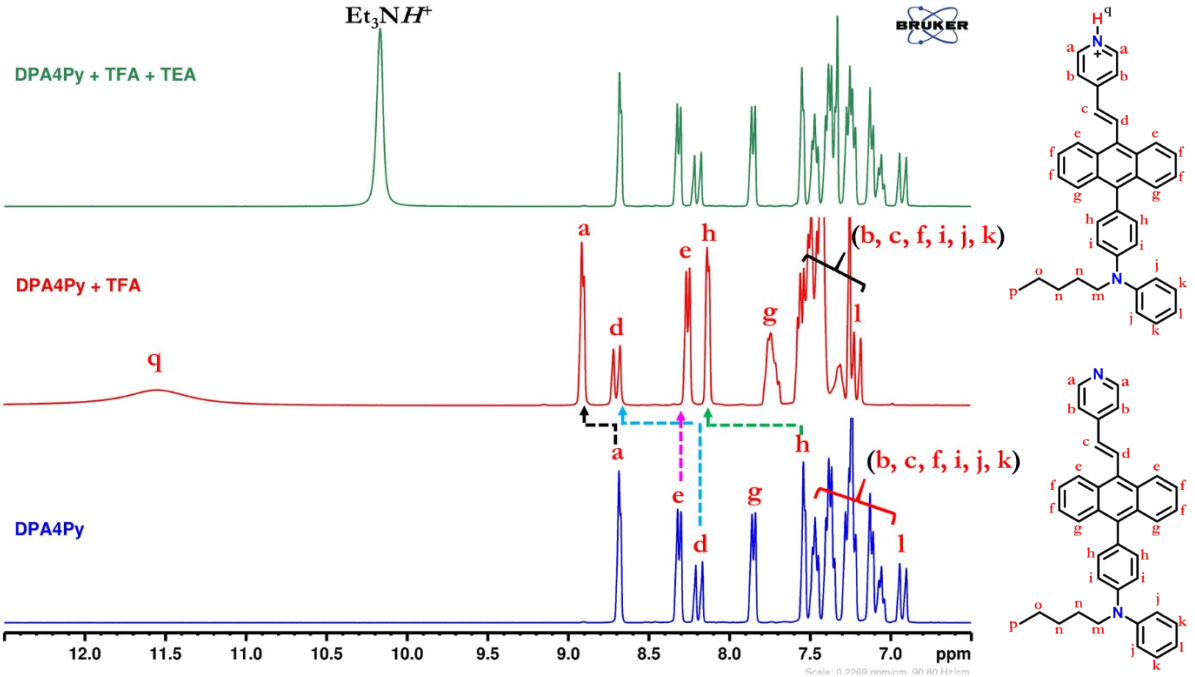



**Fig S23**: $^{1}$H NMR titration with TFA/TEA for **DPA4Py** in $CDCl_3$ (for aromatic protons)

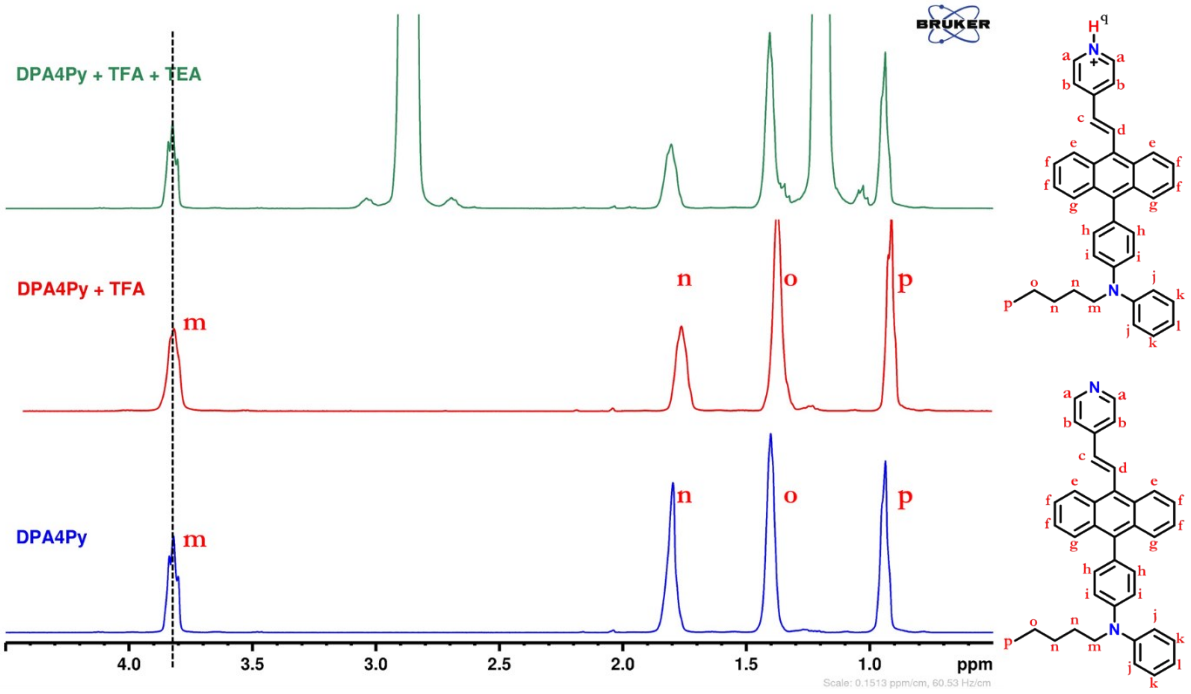



**Fig S24**: $^{1}$H NMR titration with TFA/TEA for **DPA4Py** in $CDCl_3$ (for aliphatic protons)

**Table-S4:** Lifetime parameters for **CBZ4Py**, **DPA4Py-B** and **DPA4Py-G** in their solid-states

| Probes | States | $\tau_1$ | $\tau_2$ | $\tau_3$ | $A_1$ | $A_2$ | $A_3$ | Avg. LT($\tau$/ns) | $\chi^2$ |
|---|---|---|---|---|---|---|---|---|---|
| **CBZ4Py** | Pristine | 0.36 | 1.56 | 3.51 | 0.11 | 0.70 | 0.19 | **1.80** | 1.1 |
| | Ground | 0.31 | 1.45 | 3.08 | 0.46 | 0.46 | 0.08 | **1.06** | 1.06 |
| | Annealed | 0.71 | 0.15 | 2.15 | 0.47 | 0.36 | 0.07 | **0.74** | 1.1 |
| | Protonated | 0.46 | 1.74 | 4.59 | 0.15 | 0.69 | 0.16 | **2.01** | 1.0 |
| **DPA4Py-B** | Pristine | 0.41 | 2.43 | 8.99 | 0.47 | 0.50 | 0.03 | **1.59** | 1.12 |
| | Ground | 1.07 | 3.06 | 10.99 | 0.49 | 0.49 | 0.02 | **2.24** | 1.10 |
| | Annealed | 0.44 | 3.06 | 11.42 | 0.37 | 0.60 | 0.03 | **2.31** | 1.20 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Protonated | 3.50 | 4.19 | 6.37 | 0.46 | 0.46 | 0.08 | **4.05** | 1.11 |
| **DPA4Py-G** | Pristine | 0.38 | 2.86 | 9.10 | 0.43 | 0.53 | 0.04 | **2.02** | 1.17 |
| | Ground | 1.04 | 3.01 | 10.46 | 0.47 | 0.51 | 0.02 | **2.23** | 1.11 |
| | Annealed | 0.43 | 3.04 | 11.15 | 0.37 | 0.60 | 0.03 | **2.29** | 1.18 |
| | Protonated | 3.35 | 4.28 | 7.28 | 0.48 | 0.45 | 0.07 | **4.04** | 1.25 |

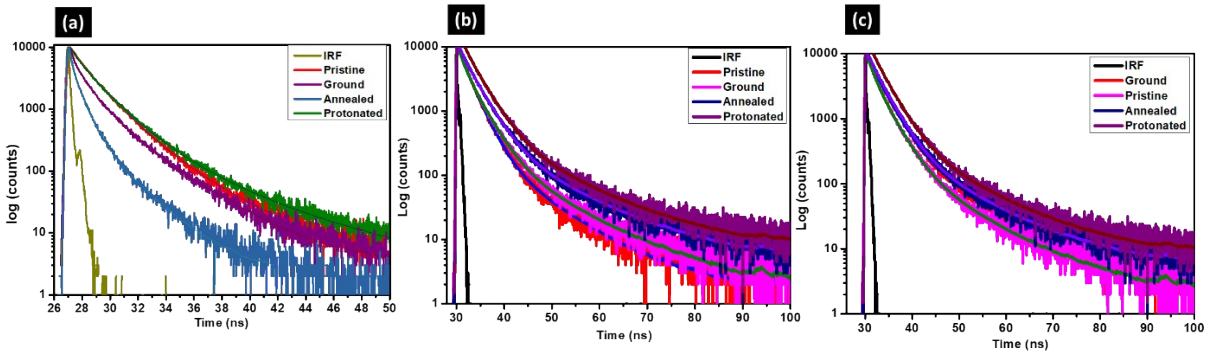



**Fig S25**: Lifetime plot for (a) **CBZ4Py**, (b) **DPA4Py-B** and (c) **DPA4Py-G**

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(1) Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria; M. A. Robb; J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian,J. V. Ortiz, A. F. Izmaylov, J. L. Williams; F. Ding; F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

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