Electronic Supplementary Information (ESI)

A Crab Claw Shaped Molecular Receptor for Selective Recognition of Picric Acid: Supramolecular Self-Assembly Mediated Aggregation Induced Emission and Color Change

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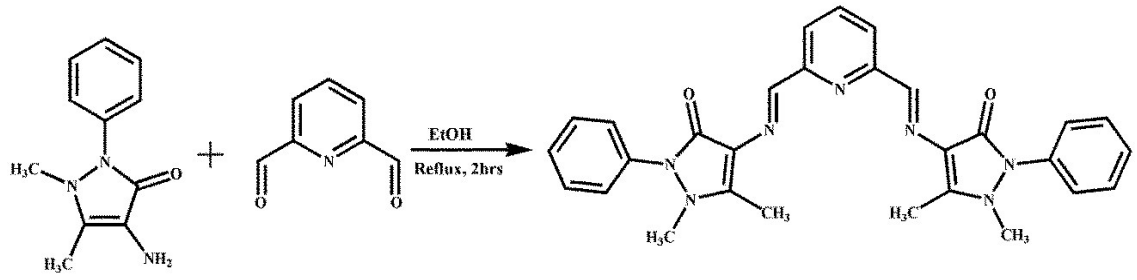
Experimental Section

1.1 Materials and methods: All other reagents and solvents were obtained from commercial suppliers (Aldrich, Alfa Aesar, and TCI Chemicals) and used as received; solvents were purified from appropriate drying agents when necessary. Absorption and fluorescence spectra were recorded using Perking Elmer Lambda 1050 and Jasco Fluorescence spectrometer-FP-8200 instruments. FT-IR spectra were measured using a Shimadzu IR Affinity-1S spectrophotometer with KBr pellets. The solid state spectra of the samples were recorded on UV-VIS spectrophotometer (SHIMADZU 01174) with barium sulfate as the reference, equipped with a diffuse reflectance accessory. The measured reflectance spectra were converted to absorption using Kubelka-Munk equation. The structure and electronic properties of PyBAP, PyBAP-PA, and PyBAP-H have been investigated by using density functional theory (DFT) and time-dependent DFT (TDDFT). TD-DFT calculations have been performed using the B3PW91 exchange correlation functional, as implemented in the Gaussian03 program package. The 6-31+G(d, p) basis set was used for N, O, C and H.

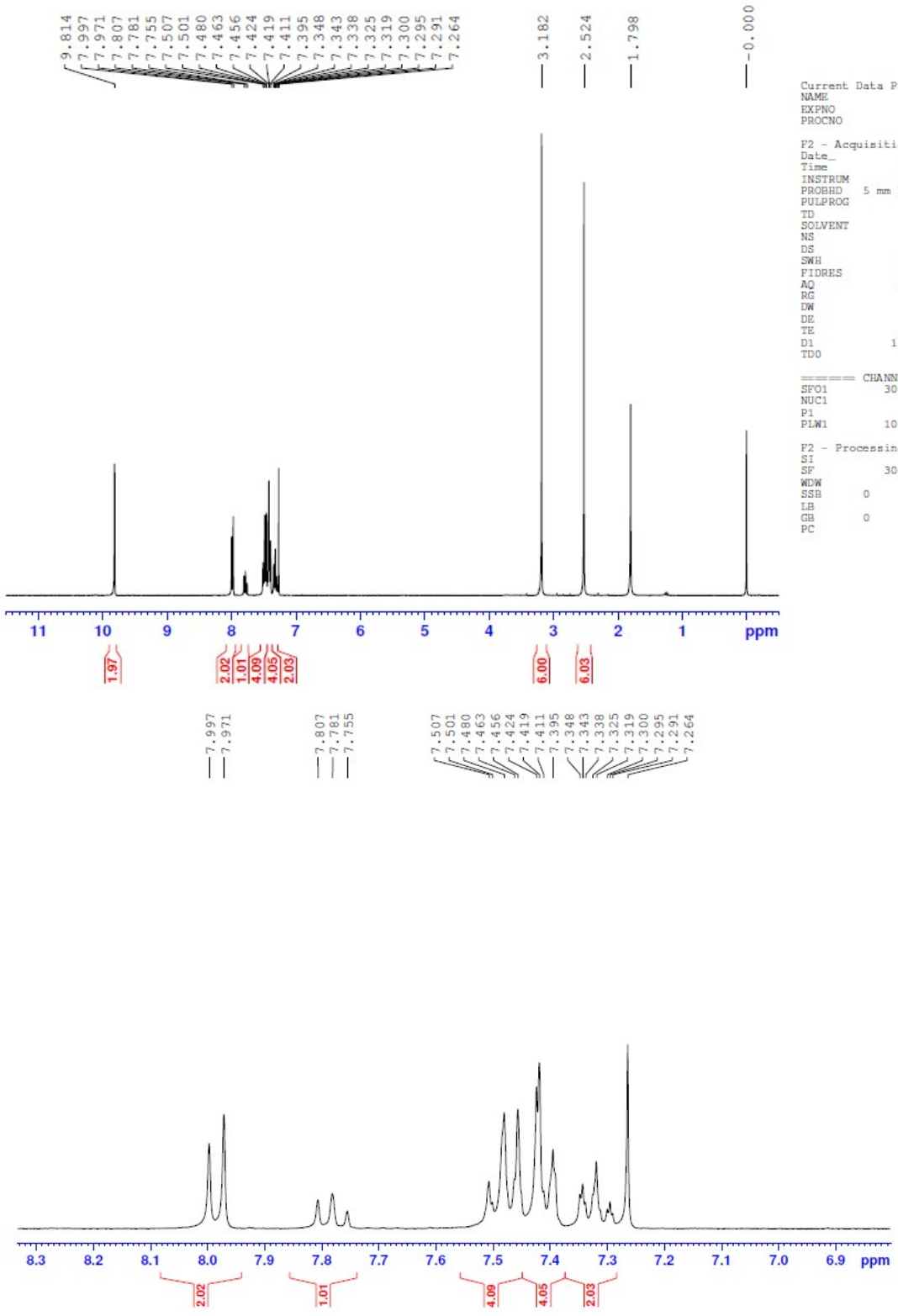
Caution! Nitroexplosives viz. TNT, RDX and PA are highly explosive and should be handled sensibly in small amounts to prevent any explosion.

1.2 Preparation of 2,6-Pyridine bis(iminoantipyrine) (PyBAP): Schiff base have been synthesized by reflux the mixture of 4-aminoantipyrine (0.3g, 1.4 mmol) with 2,6-pyridinedicarboxaldehyde (0.1g, 0.7 mmol) in 15 mL ethanol for 2h. After completion the reaction the resulting mixture was filtered, washed with ethanol and dried in a vacuum. Yield (0.257g, 68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.81 (s, 2H (imine)), 7.98 (d, J = 7.8 Hz, 2H), 7.78 (t, J = 7.8 Hz, 1H), 7.51-7.46 (m, 4H), 7.42-7.39 (m, 4H), 7.35-7.29 (m, 2H), 3.18 (s, 6H), 2.52 (s, 6H). IR (KBr): ν = 2925(m), 1640(s), 1595(s), 1551(s), 1491(s), 1412(s), 1294(m), 1136(s), 956(m), 768(m), 698(m), 563(m).



Scheme S1. Synthesis of molecular receptor 2,6-Pyridine bis(iminoantipyrine) (PyBAP).

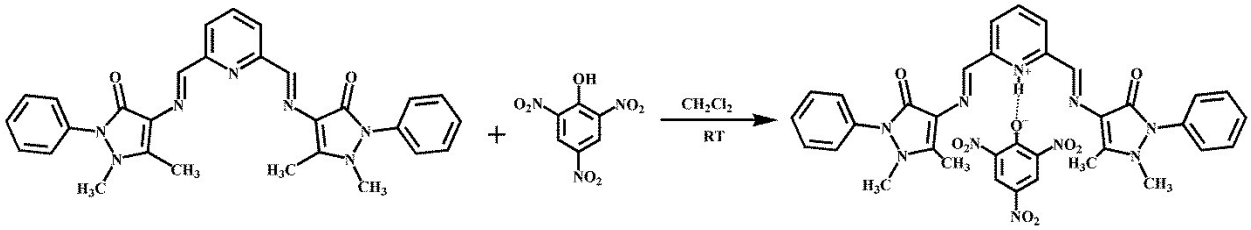
(a)



(b)

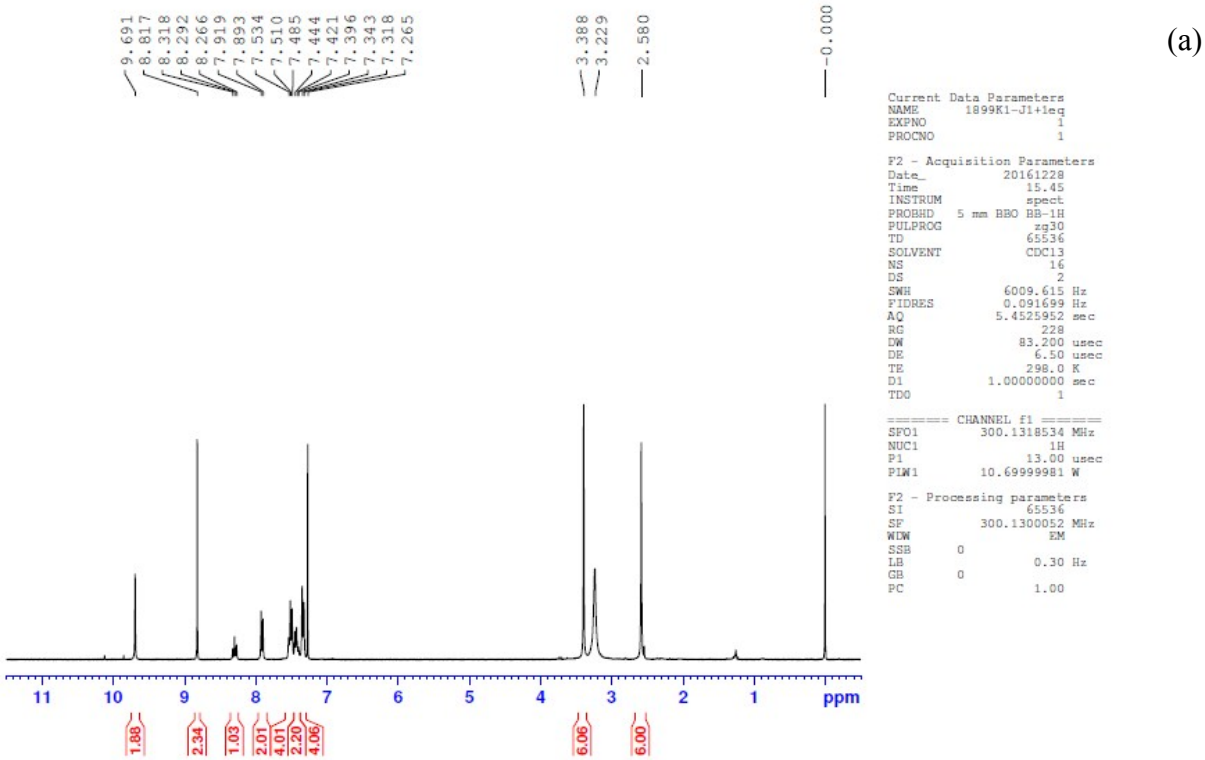
Fig. S1. (a) ^{1}H NMR spectrum for compound PyBAP and (b) expanded in the mid-range.

1.3 Preparation of PyBAP-PA: PyBAP (0.03 g, 0.059 mmol) was dissolved in dichloromethane (5 mL) and picric acid (0.0135 g, 0.059 mmol) was added into the solution that converted the colorless solution to reddish-orange immediately. The solution was stirred further at RT for 5 min. Then, diethyl ether was allowed to diffuse in to the dichloromethane solution for 3 days. The formed red crystals were washed with diethyl ether and isolated carefully, Yield (0.040 g, 94 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (s, 2H (imine)), 8.82 (s, 2H), 8.29 (t, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.53-7.48 (m, 4H), 7.44-7.39 (m, 2H), 7.33 (d, *J* = 7.5 Hz, 4H), 3.39 (s, 6H), 2.58 (s, 6H). IR spectrum (KBr) ν = 3088(m), 1650(m0, 1610(s), 1497(s), 1397(s), 1297(s), 1150(s), 1061(m), 751(m), 697(m).



Scheme S2. Synthesis of host-guest complex PyBAP-PA.

(a)



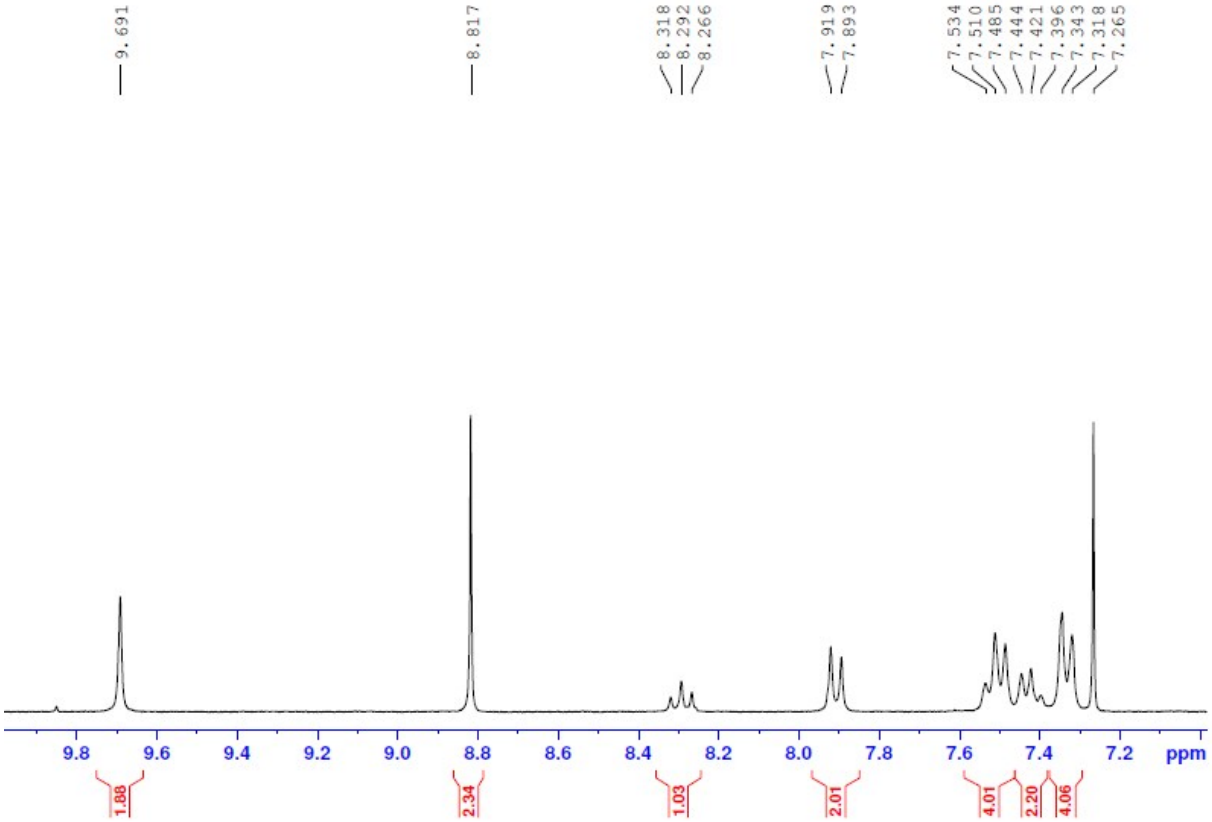


Fig. S2. (a) ^{1}H NMR spectrum for compound PyBAP-PA and (b) expanded in the mid-range.

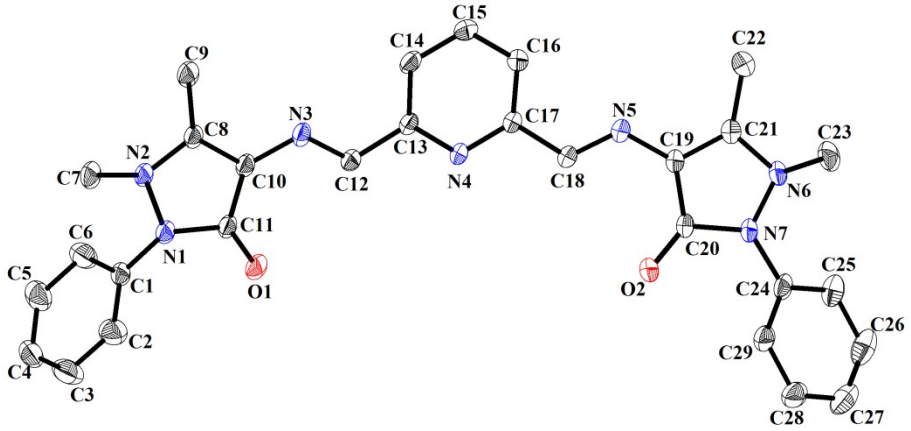


Fig. S3 ORTEP diagram of PyBAP with 50% probability ellipsoid with atom label. H-atoms are omitted for clarity. Color code: carbon - grey, oxygen - red, nitrogen – blue.

Table S1. Crystal data and structure refinement for PyBAP (CCDC 1534731)

Identification code	SPA157	
Empirical formula	$C_{29}H_{27}N_7O_2$	
Formula weight	505.57	
Temperature	173(2) K	
Wavelength	0.610 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.307(2) Å	α= 90°.
	b = 21.037(2) Å	β= 101.561(3)°.
	c = 13.607(2) Å	γ = 90°.
Volume	2610.1(7) $Å^3$	
Z	4	
Density (calculated)	1.287 Mg/m^3	
Absorption coefficient	0.062 mm^{-1}	
F(000)	1064	
Crystal size	0.325 x 0.311 x 0.295 mm^3	
Theta range for data collection	1.552 to 25.000°.	
Index ranges	-12<=h<=12, -29<=k<=29, -18<=l<=18	
Reflections collected	14320	
Independent reflections	7258 [R(int) = 0.0240]	
Completeness to theta = 21.469°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.860	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7258 / 0 / 348	
Goodness-of-fit on F^2	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.1120	
R indices (all data)	R1 = 0.0594, wR2 = 0.1193	
Extinction coefficient	0.038(3)	
Largest diff. peak and hole	0.379 and -0.218 $e.Å^{-3}$	

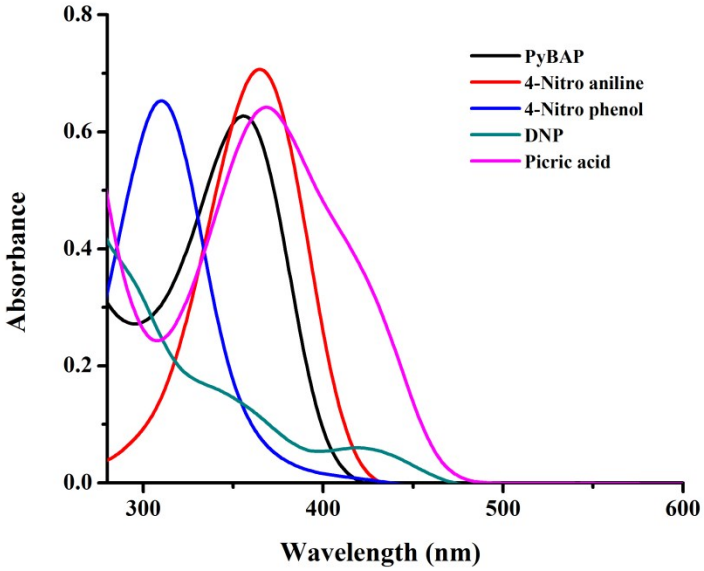


Fig. S4 Absorption spectra of PyBAP and different nitroaromatic compounds (10^{-3} M).

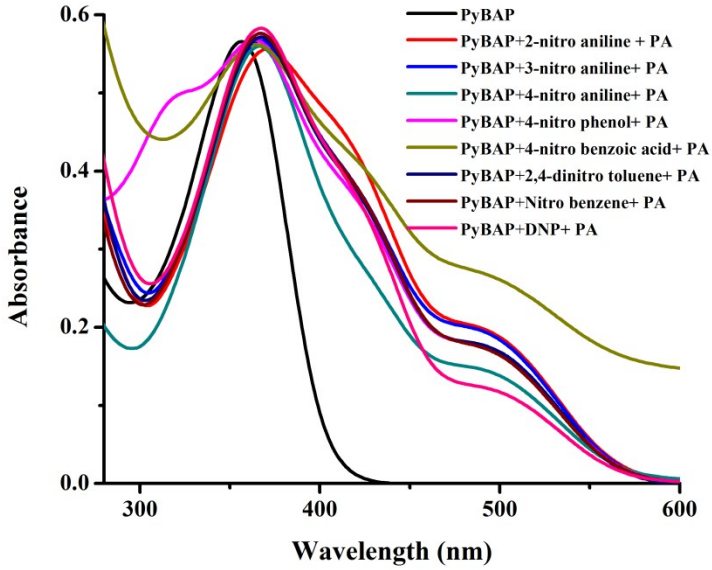


Fig. S5 Absorption spectra of PyBAP (10^{-3} M) with different aromatic aniline and picric acid (10^{-3} M).

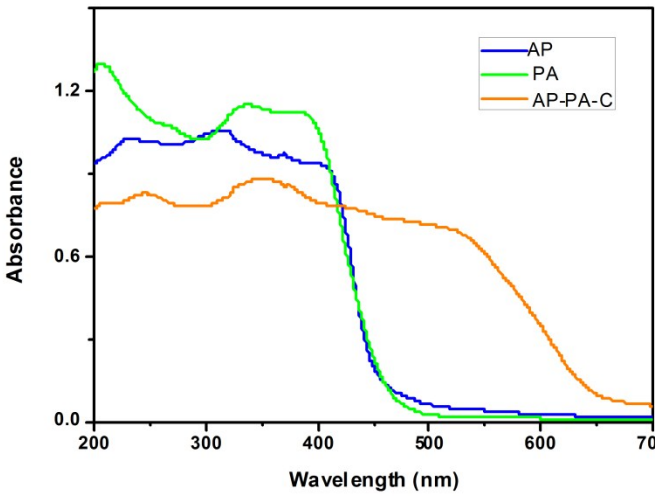


Fig. S6 Solid state absorption spectra of PyBAP, PA and PyBAP-PA

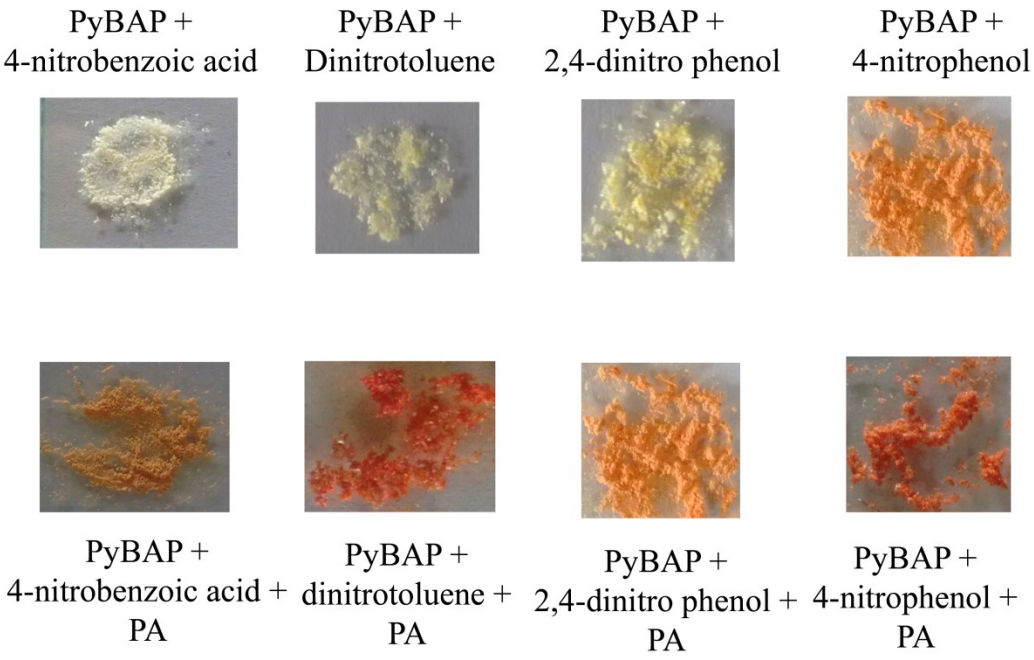


Fig. S7 Digital images: Color NACs with PyBAP receptor (top row). Color of NACs with PyBAP in the presence of PA (bottom row).

Table S2. Crystal data and structure refinement for PyBAP-PA (CCDC 1534730)

Identification code	SPA156	
Empirical formula	$C_{35}H_{30}N_{10}O_9$	
Formula weight	734.69	
Temperature	173(2) K	
Wavelength	0.630 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.689(2) Å	α= 90°.
	b = 21.090(3) Å	β= 93.045(4)°.
	c = 15.168(2) Å	γ = 90°.
Volume	3414.5(9) $Å^3$	
Z	4	
Density (calculated)	1.429 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	1528	
Crystal size	0.112 x 0.095 x 0.085 mm^3	
Theta range for data collection	1.467 to 25.999°.	
Index ranges	-14<=h<=14, -29<=k<=29, -21<=l<=21	
Reflections collected	18995	
Independent reflections	9628 [R(int) = 0.0355]	
Completeness to theta = 22.210°	99.7 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.836	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9620 / 12 / 493	
Goodness-of-fit on F^2	0.992	
Final R indices [I>2sigma(I)]	R1 = 0.0629, wR2 = 0.2287	
R indices (all data)	R1 = 0.1139, wR2 = 0.2541	
Extinction coefficient	0.037(4)	
Largest diff. peak and hole	1.004 and -0.639 $e.Å^{-3}$	

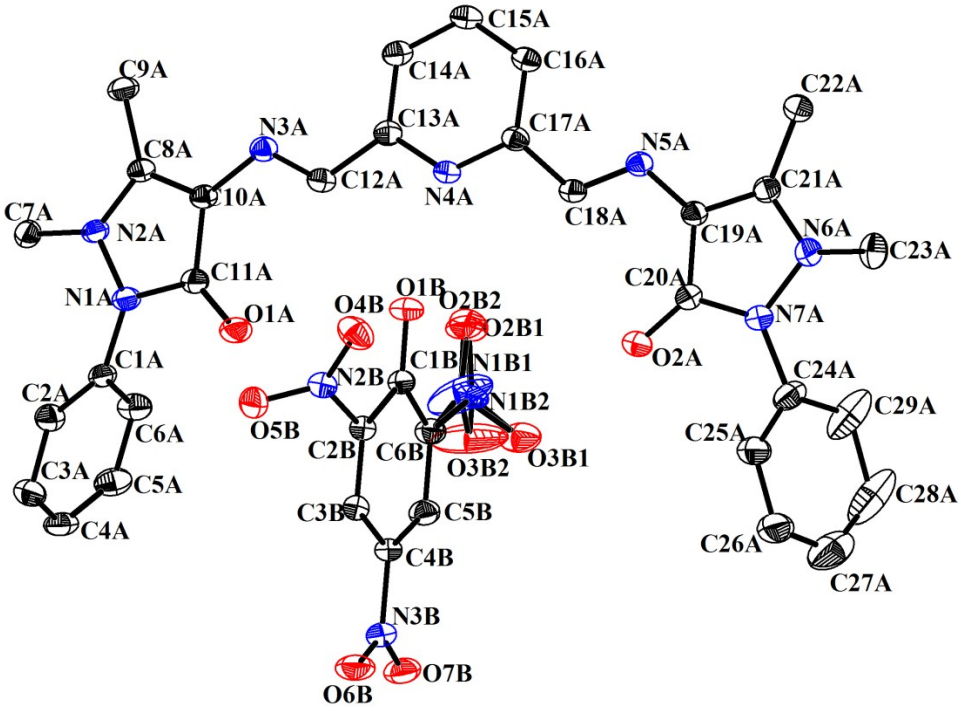


Fig. S8 ORTEP diagram of PyBAP-PA with 30% probability ellipsoid with atom label. H-atoms are omitted for clarity. Color code: carbon - grey, oxygen - red, nitrogen – blue.

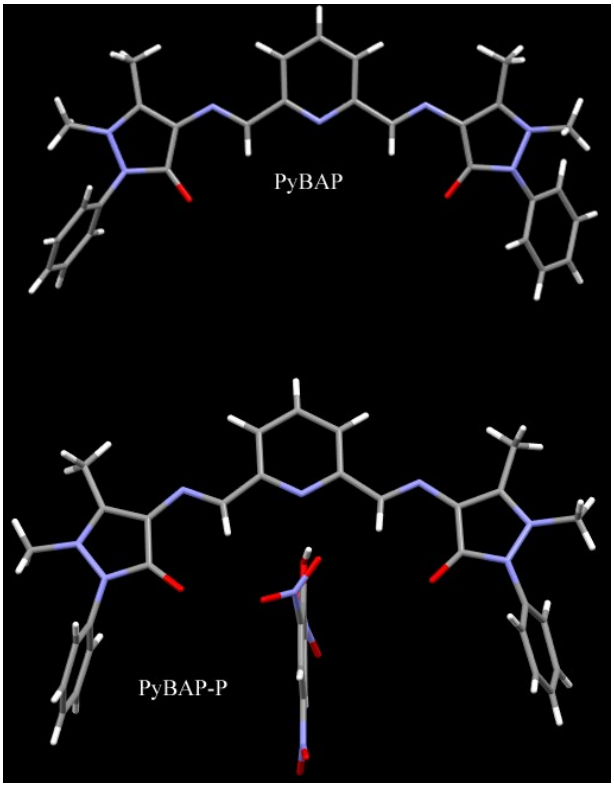


Fig. S9. Molecular structure of PYBAP and PYBAP-PA in a crystal lattice.

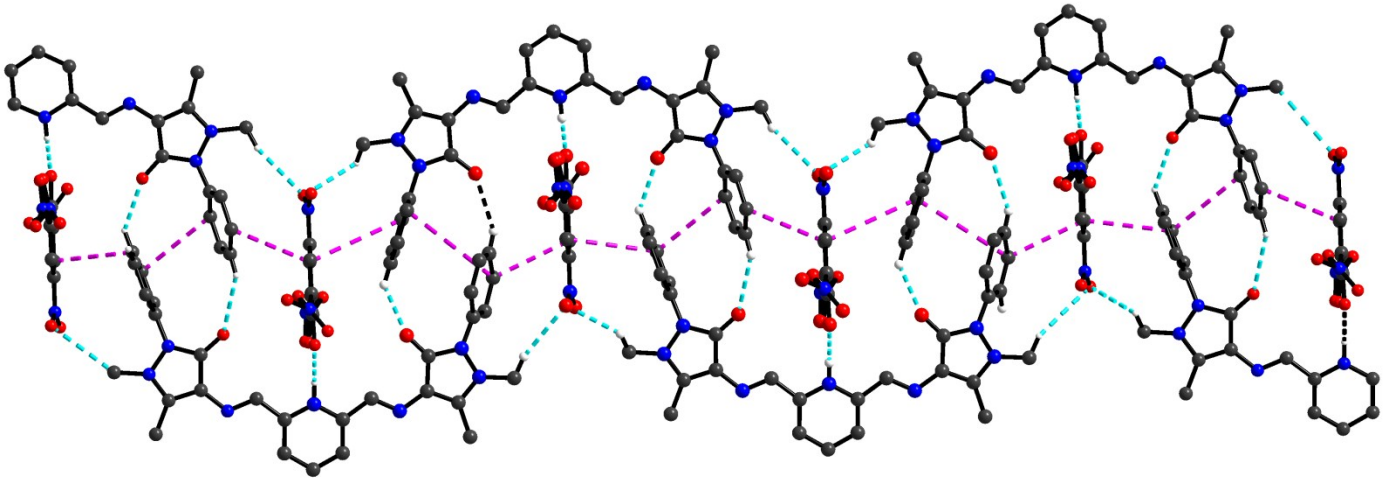


Fig. S10. The hydrogen-bond and π–π interactions in PyBAP-PA complex (hydrogen-bond= cyan line; π–π interaction=purple line). Some hydrogen atoms are omitted for clarity.

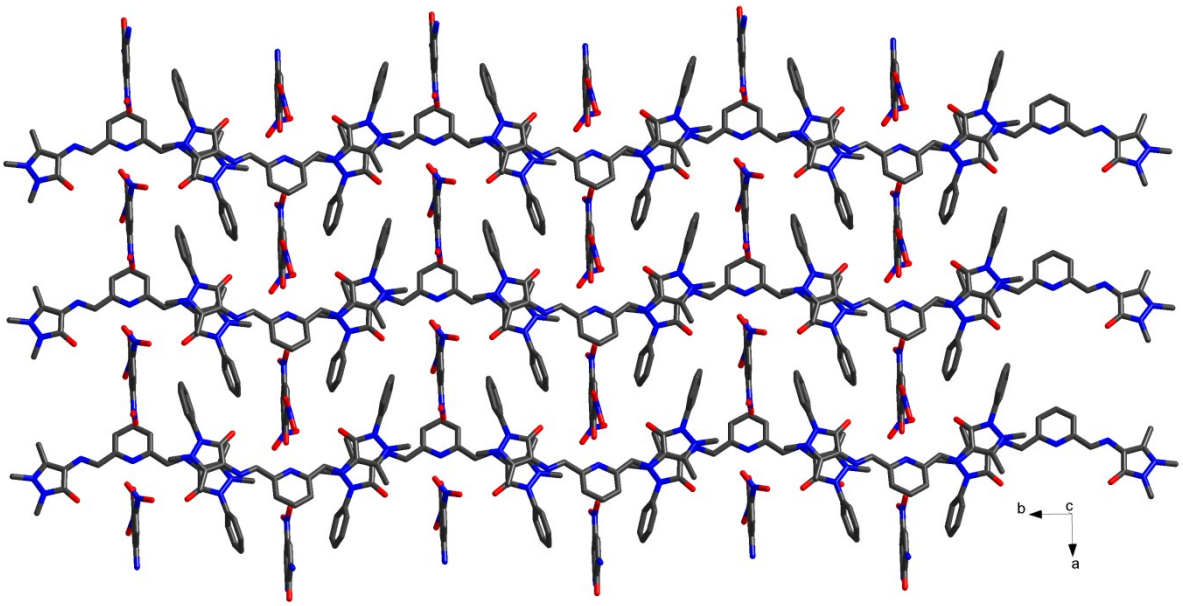


Fig. S11. The antipyrine phenyl group of PyBAP molecules are interdigitated between PA and PyBAP antipyrine phenyl along c-axis

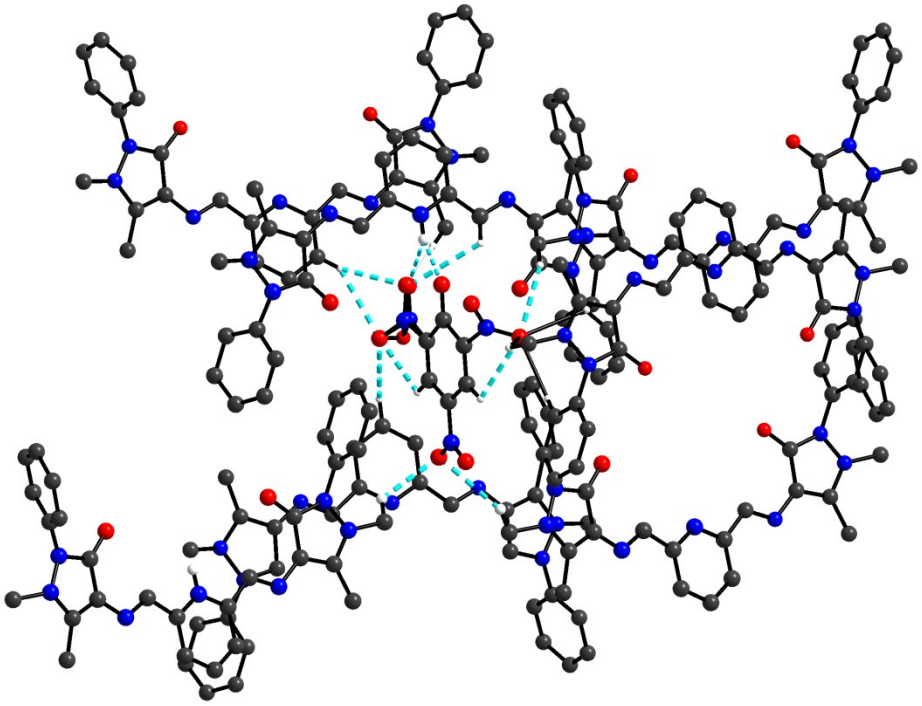


Fig. S12 Hydrogen bonding interaction between one PA and seven PyBAP receptor.

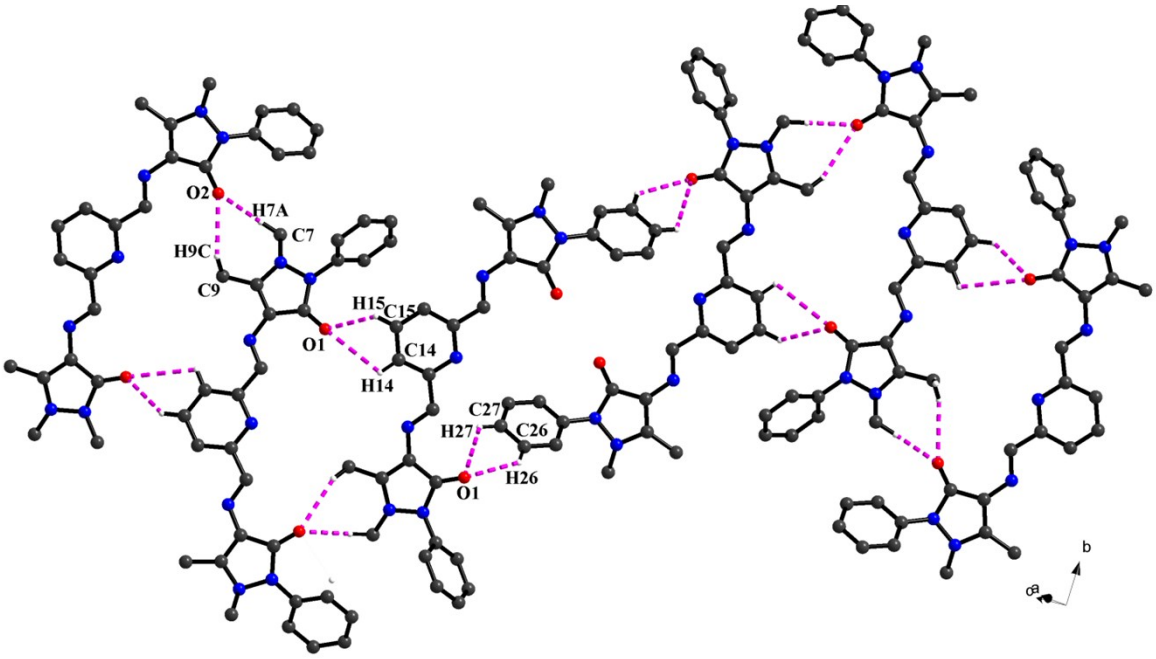


Fig. S13 C−H···O hydrogen-bonding interactions in PyBAP crystal lattice (the hydrogen-bond interactions are indicated with purple lines). Selected D−H···A and D···A distances: C26−H26···O1=2.760(2) Å, C26···O1=3.497(1) Å, C27−H27···O1=3.112(2) Å, C27···O1=3.667(1) Å, C14−H14···O1=3.105(4)Å, C14···O1=3.534(5) Å, C15−H15···O1=2.501(1) Å, C15···O1=3.238(3) Å, C17−H7A···O2=2.329(3) Å, C7···O2=3.287(5) Å, C9−H9C···O2=2.621(0) Å, C9···O2=3.471(1) Å.

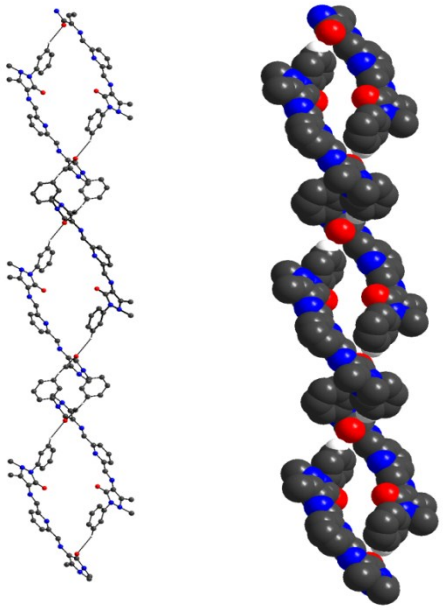


Fig. S14 Crystal packing of PyBAP showing the helical arrangement due to C−H···O hydrogen-bonding interactions.

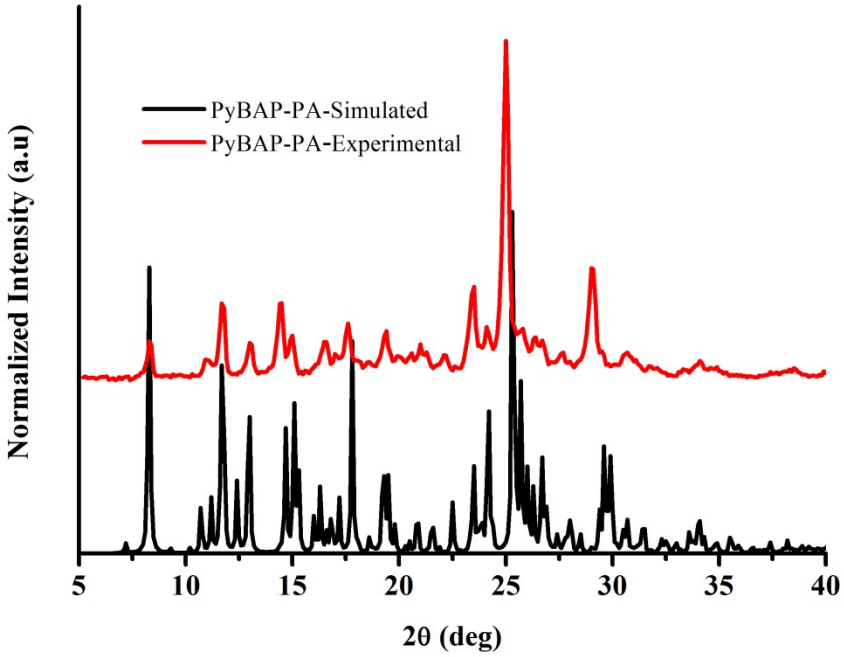


Fig. S15. Experimental and simulated PXRD pattern of PyBAP-PA.

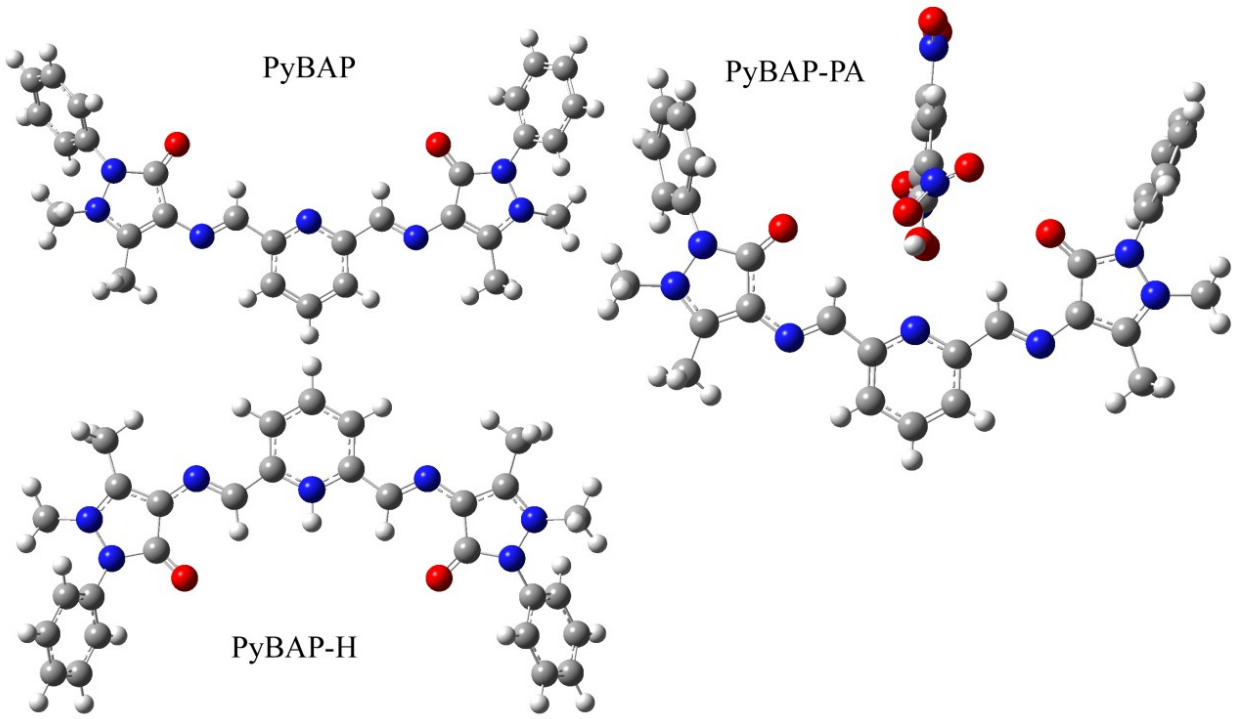


Fig. S16. Optimized structure of PyBAP, PyBAP-PA and PyBAP-H.

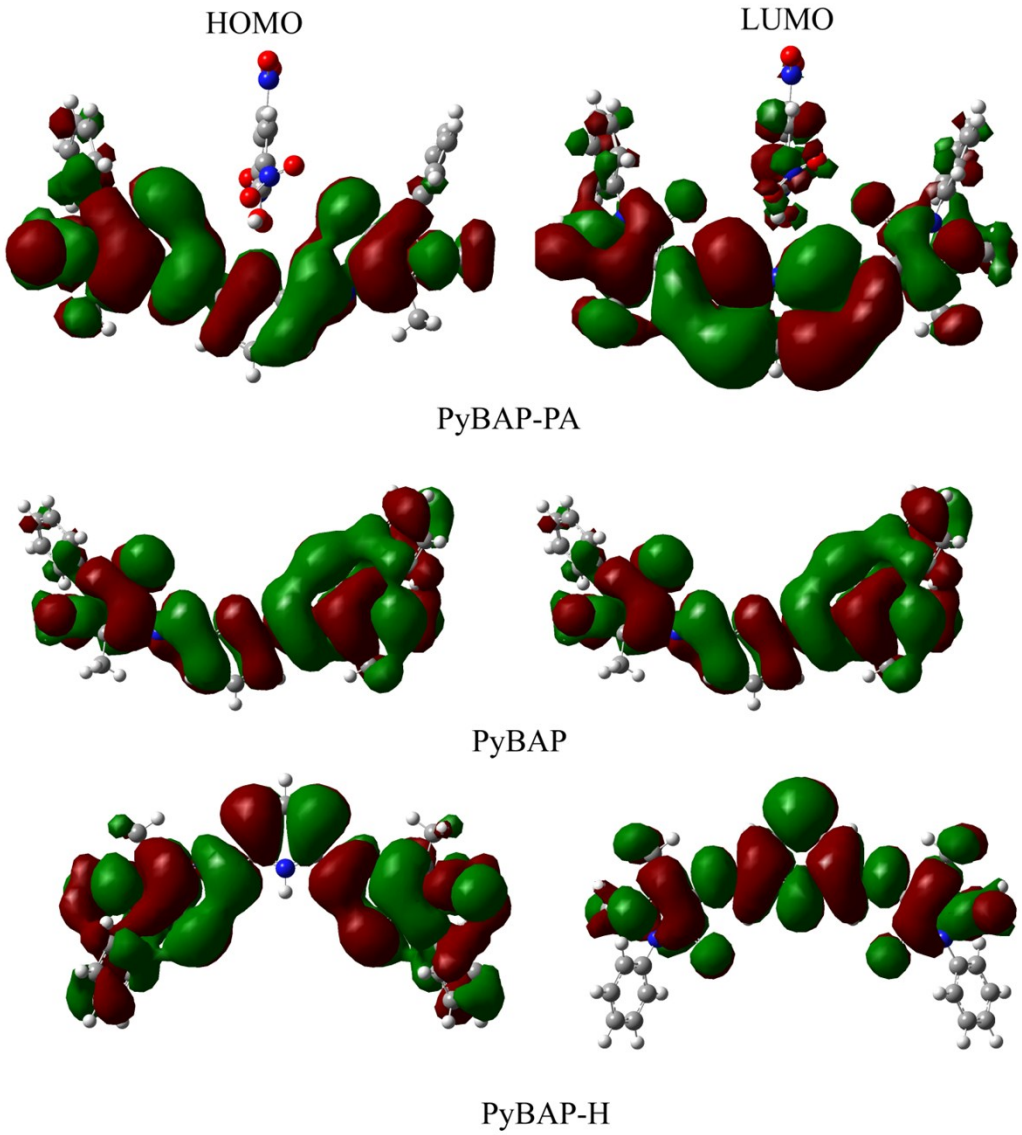


Fig. S17. Molecular orbital plots of the HOMOs and LUMOs of PyBAP-PA, PyBAP and PyBAP-H.

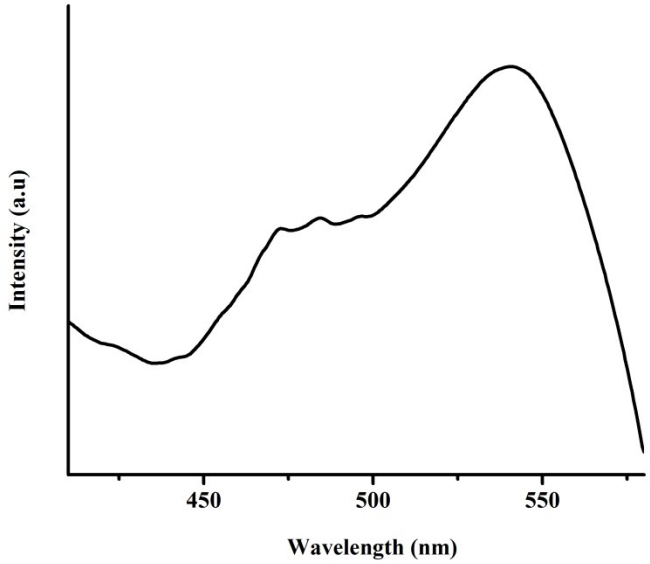


Fig. S18. The excitation spectra of PyBAP-PA.

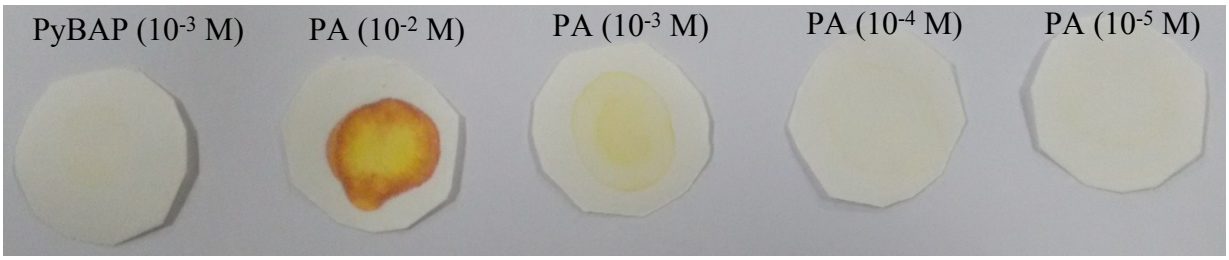


Fig. S19. PyBAP paper strip dipped in different concentration of PA solution.