Supporting Information

New efficient organic scintillators derived from pyrazoline

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NMR analysis

All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECX-300 spectrometer operating at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR at room temperature and in $CDCl_3$ solvent. The chemical shifts (δ) are reported in ppm and were referenced to the residual solvent peak. The coupling constants (J) are quoted in Hz.

NMR 1H spectra

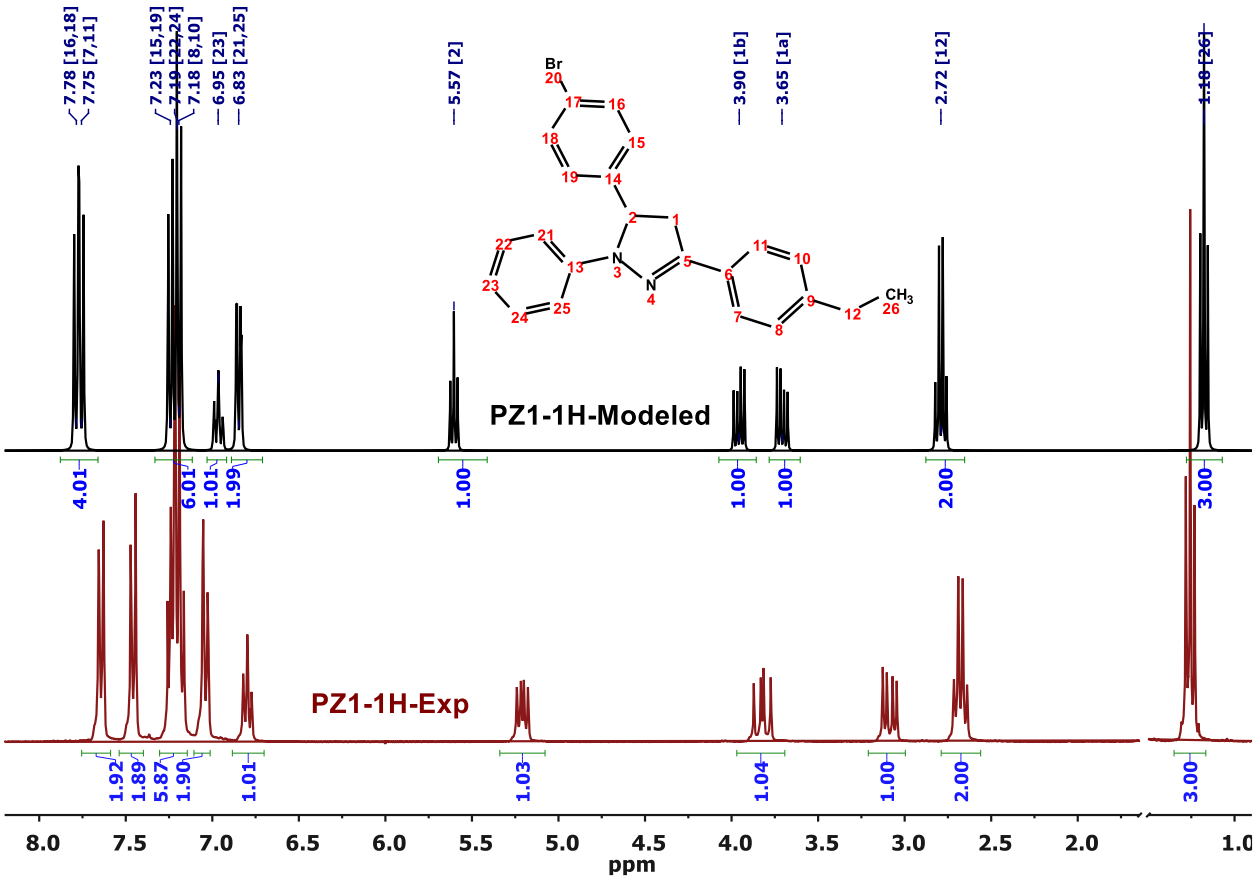

Figure S1. 1H NMR spectra for the modeled structure of 5-(4-bromophenyl)-3-(4-ethylphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (PZ1) (black) and the corresponding experimental results (dark red) in deuterated chloroform ($CDCl_3$). The modeled results of 1H NMR (300 MHz, Chloroform) show proton chemical shift values of δ 7.77 (d, J = 9.0 Hz, 4H), 7.32-7.10 (m, 6H), 6.95 (s, 1H), 6.83 (s, 2H), 5.57 (s, 1H), 3.90 (s, 1H), 3.65 (s, 1H), 2.72 (s, 2H), 1.18 (s, 3H). The experimental 1H NMR spectrum show two peaks at 1.35-1.17 and 2.68 corresponding to the 3 and the 2 protons of the ethyl side group attached to one of the phenyl ring. The 3 protons of the pyrazole group appeared as three peaks between 3.0 and 5.5 ppm. The integration of the modeled and the experimental NMR gives almost the same number of protons.

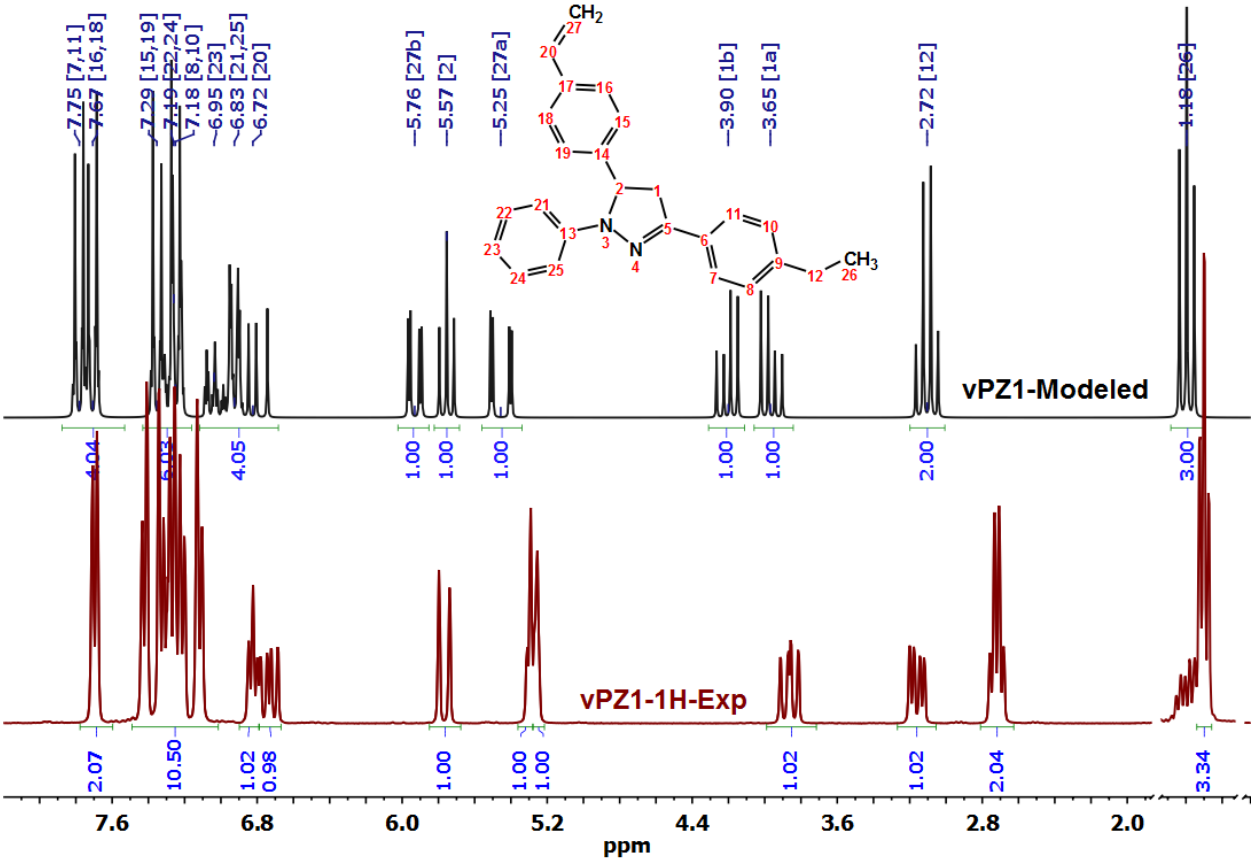

Figure S2. 1H NMR spectra for the modeled structure of 3-(4-ethylphenyl)-5-(4-vinylphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (vPZ1) (black) and the corresponding experimental results (dark red) in deuterated chloroform ($CDCl_3$). The modeled results of 1H NMR (300 MHz, Chloroform) show proton chemical shift values of 1H NMR (300 MHz, Chloroform) δ 7.71 (d, J = 24.0 Hz, 4H), 7.37-7.08 (m, 6H), 7.04-6.57 (m, 4H), 5.76 (s, 1H), 5.57 (s, 1H), 5.25 (s, 1H), 3.90 (s, 1H), 3.65 (s, 1H), 2.72 (s, 2H), 1.18 (s, 3H). The experimental 1H NMR spectrum of the vPZ1 shows new three peaks between 5 and 6.75 ppm: two peaks at 5.25 and 5.77 ppm assigned to the chemical shift of hydrogen in -CH_2 of the vinyl group and one peak at 6.73 ppm assigned to the –CH proton of the same vinyl group. The integration of the modeled and the experimental NMR gives almost the same number of protons.

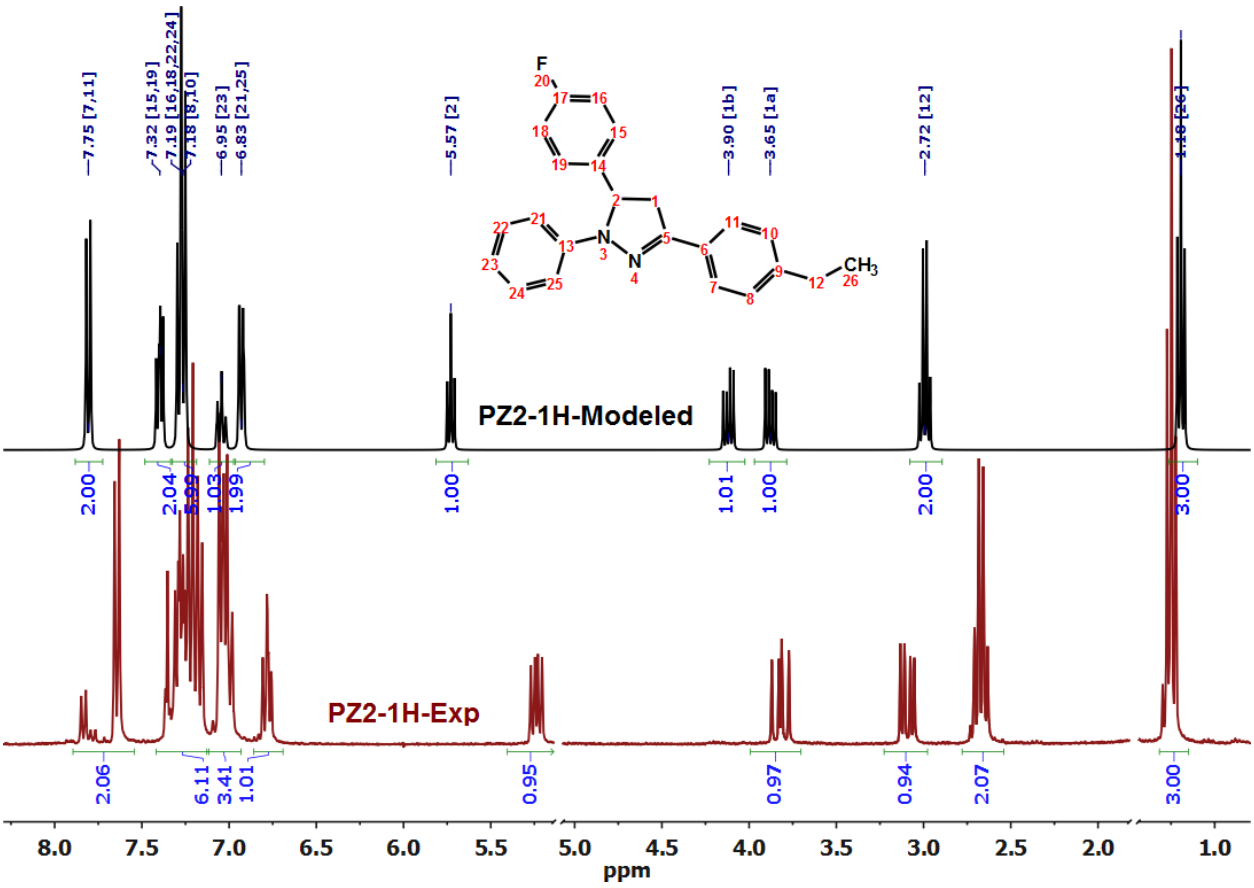

Figure S3. 1H NMR spectra for the modeled structure of 3-(4-ethylphenyl)-5-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (PZ2) (black) and the corresponding experimental results (dark red) in deuterated chloroform ($CDCl_3$). The modeled results of 1H NMR (300 MHz, Chloroform) show proton chemical shift values of 1H NMR (300 MHz, Chloroform) δ 7.75 (s, 2H), 7.32 (s, 2H), 7.18 (d, J = 3.0 Hz, 6H), 6.95 (s, 1H), 6.83 (s, 2H), 5.57 (s, 1H), 3.90 (s, 1H), 3.65 (s, 1H), 2.72 (s, 2H), 1.18 (s, 3H). The experimental 1H NMR spectrum show two peaks at 1.32-1.15 and 2.78-2.54 corresponding to the 3 and the 2 protons of the ethyl side group attached to one of the phenyl ring. The 3 protons of the pyrazole group appeared as three peaks between 3.0 and 5.5 ppm. The integration of the modeled and the experimental NMR gives almost the same number of protons. The NMR of PZ2 is similar to that of PZ1 with small shift due to the difference between the Br and F atoms.

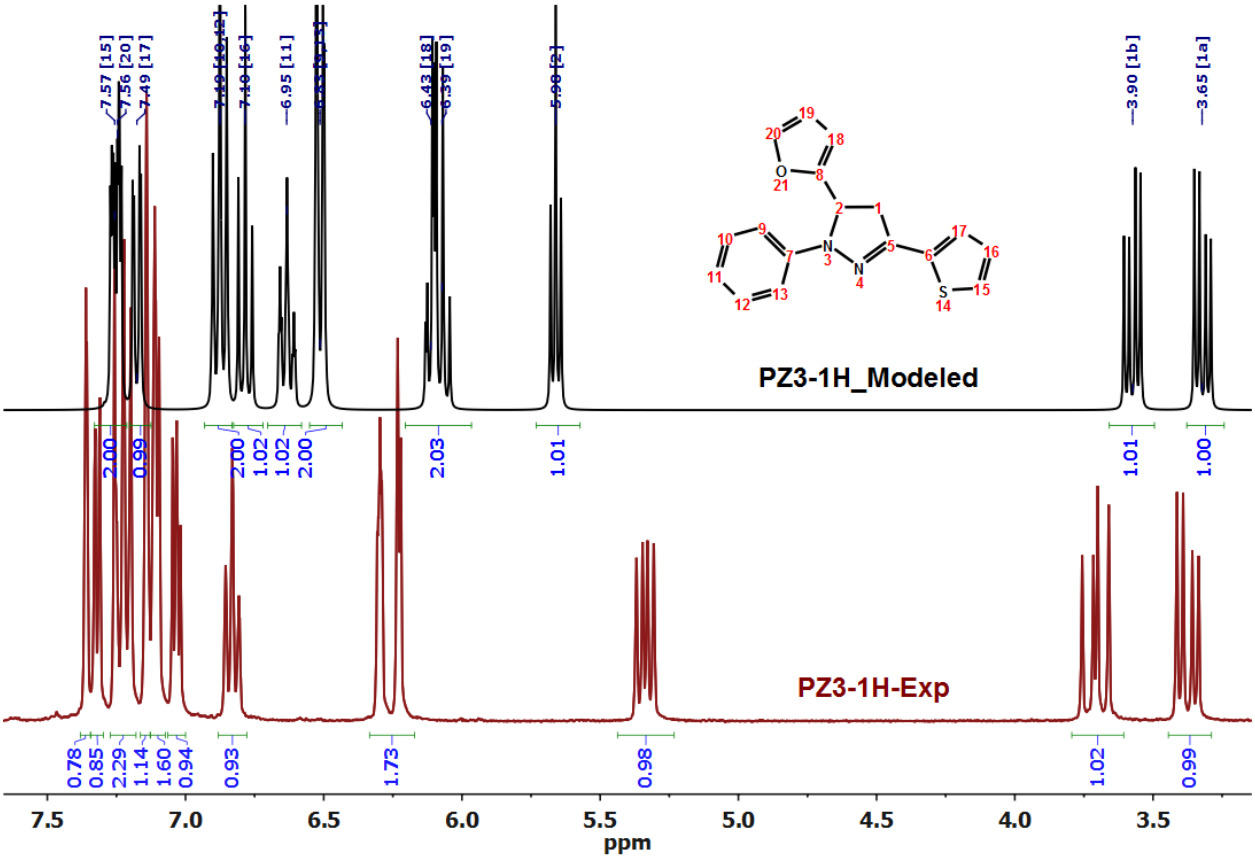

Figure S4. 1H NMR spectra for the modeled structure of 5-(furan-2-yl)-1-phenyl-3-(thiophen-2-yl)-4,5-dihydro-1H-pyrazole (PZ3) (black) and the corresponding experimental results (dark red) in deuterated chloroform ($CDCl_3$). The modeled results of 1H NMR (300 MHz, Chloroform) show proton chemical shift values of 1H NMR (300 MHz, Chloroform) 1H NMR (300 MHz, Chloroform) δ 7.57 (d, J = 3.0 Hz, 2H), 7.49 (s, 1H), 7.19 (s, 2H), 7.10 (s, 1H), 6.95 (s, 1H), 6.83 (s, 2H), 6.41 (d, J = 12.0 Hz, 2H), 5.98 (s, 1H), 3.90 (s, 1H), 3.65 (s, 1H). The experimental 1H NMR spectrum of PZ3 shows that the three peaks assigned to the chemical shift of 3 protons in pyrazole group appear at 3.37, 3.71 and 5.34 ppm. Two protons of the furan group appear at 6.28 ppm, while the peak at 7.14 ppm assigned to one proton of the thiophene group. The 5 protons assigned for the phenyl group are between 6.75 and 7.5 ppm. The result is different from the other three materials because PZ3 has three different cyclic groups, which have specific peaks positions.

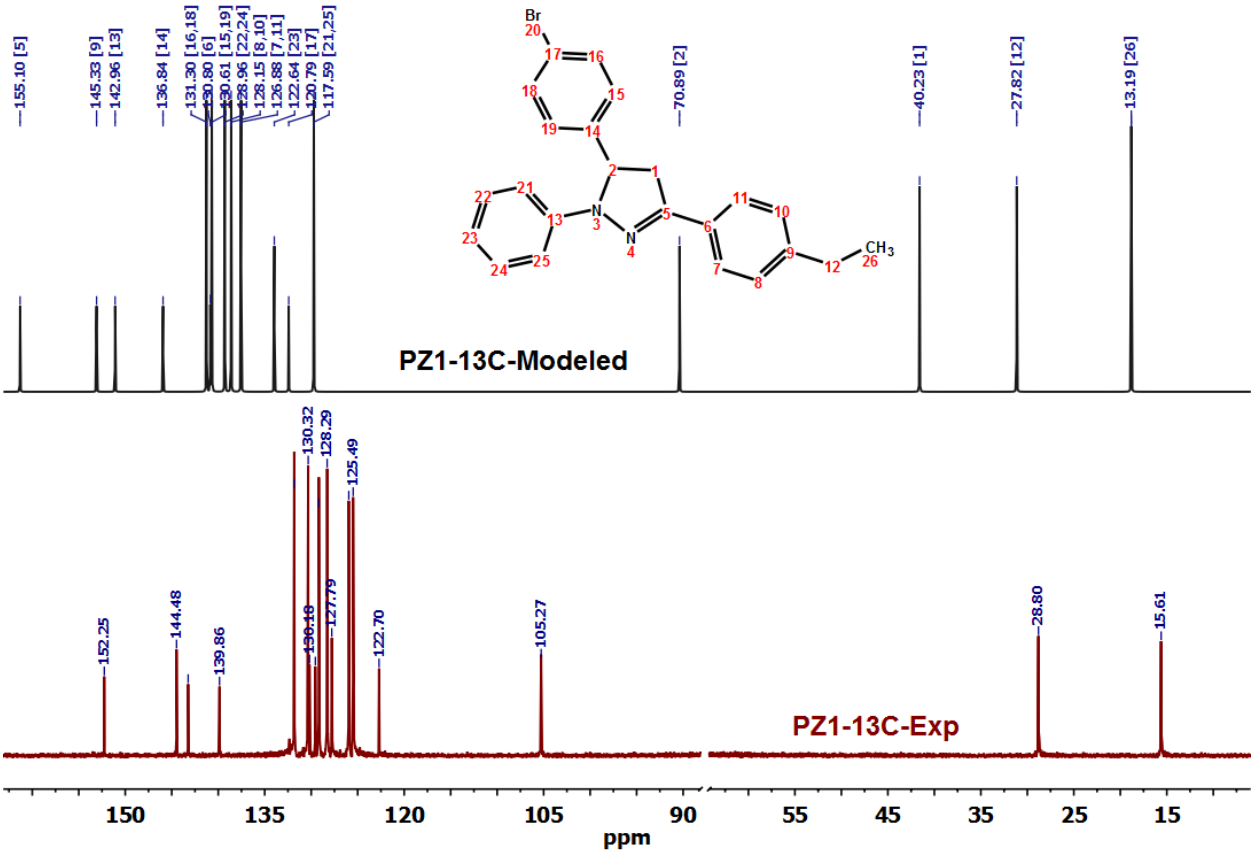

Figure S5. 13C NMR spectra for the modeled structure of 5-(4-bromophenyl)-3-(4-ethylphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (PZ1) (black) and the corresponding experimental results (dark red) in deuterated chloroform ($CDCl_3$). The modeled results of 13C NMR (75 MHz, Common NMR Solvents) δ 155.10 (s), 145.33 (s), 142.96 (s), 136.84 (s), 131.30 (s), 130.71 (d, *J* = 14.6 Hz), 128.96 (s), 128.15 (s), 126.88 (s), 122.64 (s), 120.79 (s), 117.59 (s), 70.89 (s), 40.23 (s), 27.82 (s), 13.19 (s). The experimental 13C NMR spectrum of PZ1 shows that the ethyl group carbons appear as two peaks around 15.6 ppm for $–CH_3$ and 28.8 ppm $-CH_2-$ of the same group. The three carbons of the pyrazole group appear around 105.3, 122.7 and 152.3 ppm.

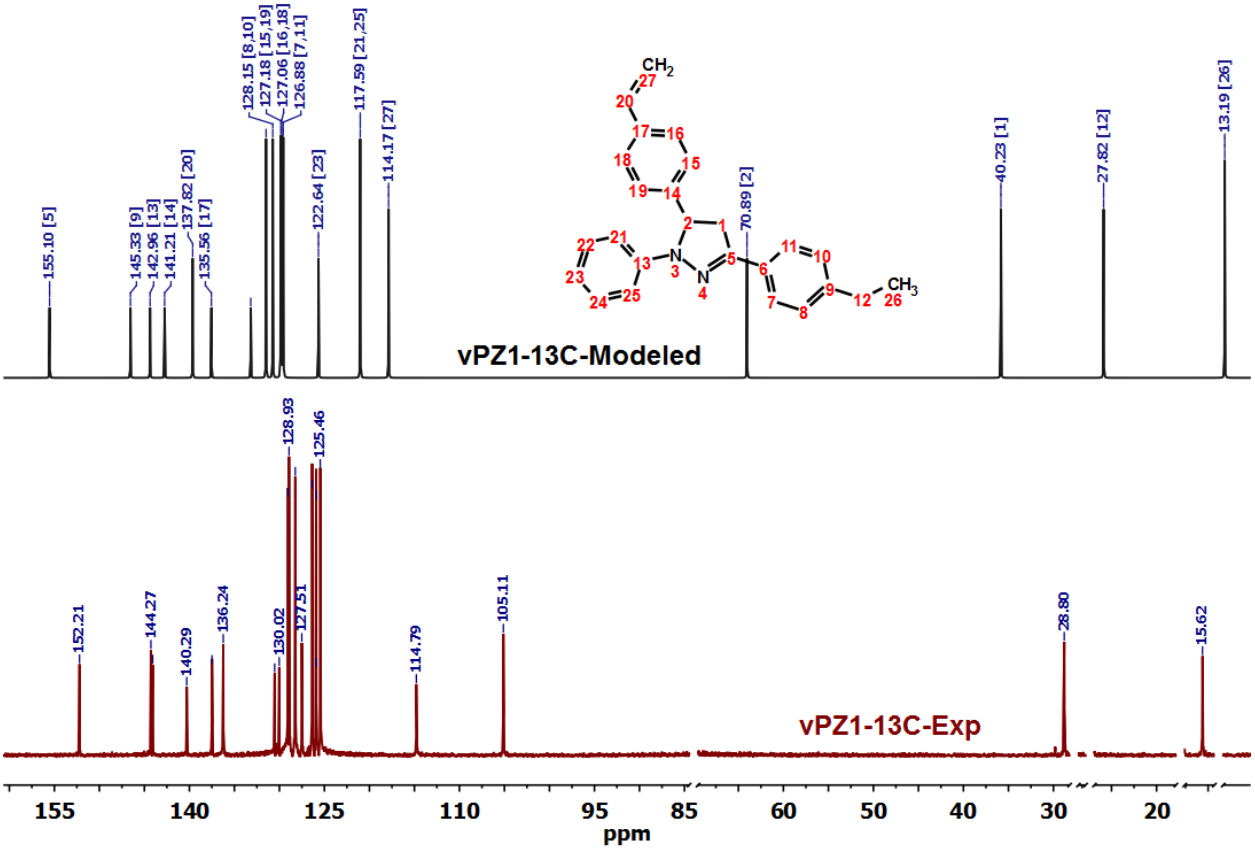

Figure S6. 13C NMR spectra for the modeled structure of 3-(4-ethylphenyl)-5-(4-vinylphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (vPZ1) (black) and the corresponding experimental results (dark red) in deuterated chloroform (CDCl3). The modeled results of 13C NMR (75 MHz, Common NMR Solvents) δ 155.10 (s), 145.33 (s), 142.96 (s), 141.21 (s), 137.82 (s), 135.56 (s), 130.80 (s), 128.96 (s), 128.15 (s), 127.38 – 126.68 (m), 122.64 (s), 117.59 (s), 114.17 (s), 70.89 (s), 40.23 (s), 27.82 (s), 13.19 (s). The experimental 13C NMR spectrum of vPZ1 shows that the ethyl group carbons appear as two peaks around 15.6 ppm for $–CH_3$ and 28.8 ppm $-CH_2-$ of the same group. The three carbons of the pyrazole group appear around 105.1, 114.8 and 152.2 ppm. The vPZ1 spectrum shows two new peaks at 125.5 and 137.5 ppm assigned to the attached vinyl group and assigned to $-CH_2$ and -CH-, respectively.

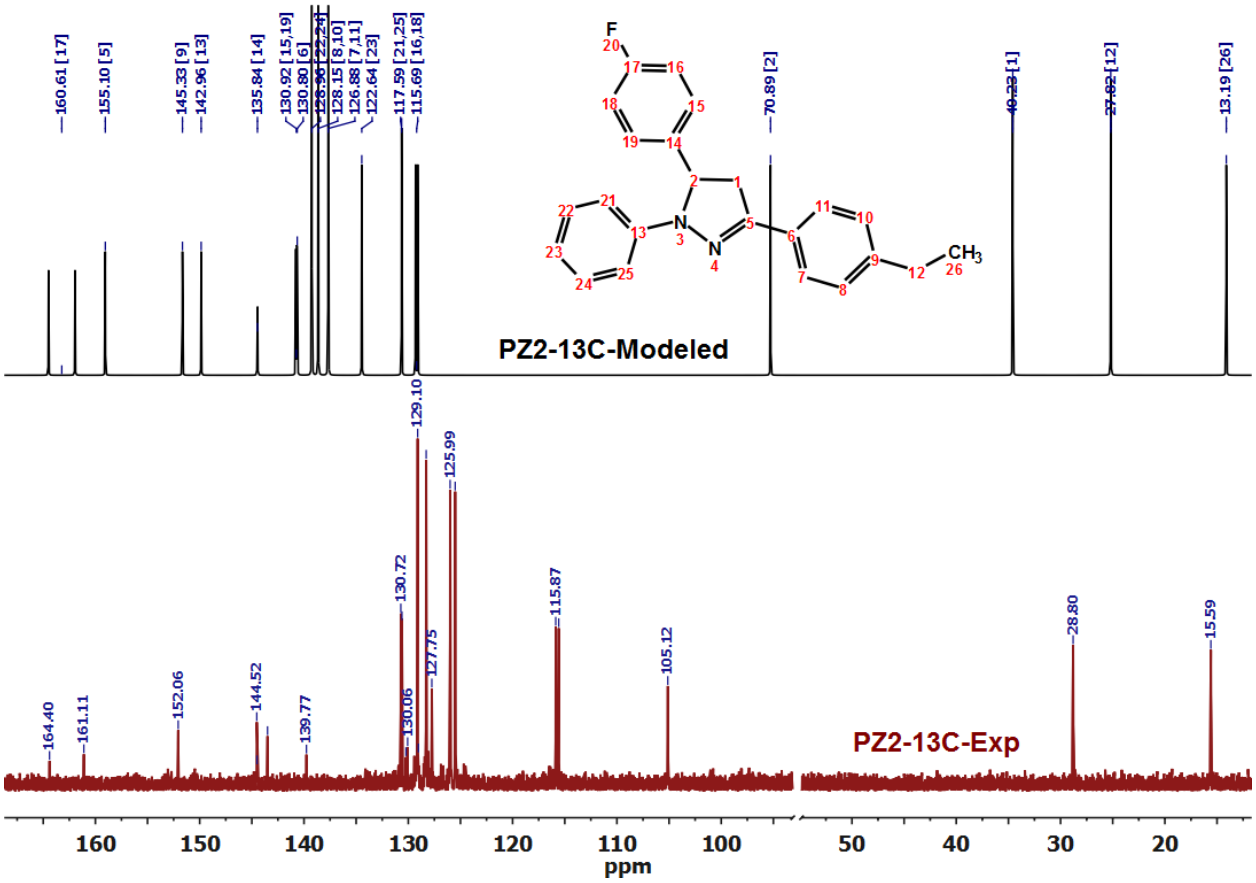

Figure S7. 13C NMR spectra for the modeled structure of 3-(4-ethylphenyl)-5-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (PZ2) (black) and the corresponding experimental results (dark red) in deuterated chloroform ($CDCl_3$). The modeled results of 13C NMR (75 MHz, Common NMR Solvents) δ 155.10 (s), 145.33 (s), 142.96 (s), 136.84 (s), 131.30 (s), 130.71 (d, *J* = 14.6 Hz), 128.96 (s), 128.15 (s), 126.88 (s), 122.64 (s), 120.79 (s), 117.59 (s), 70.89 (s), 40.23 (s), 27.82 (s), 13.19 (s). The experimental 13C NMR spectrum of PZ2 shows that the ethyl group carbons appear as two peaks around 15.6 ppm for $–CH_3$ and 28.8 ppm $-CH_2-$ of the same group. The three carbons of the pyrazole group appear around 105.1, 115.9 and 152.0 ppm. The carbon attached to the fluoride atom shows a big chemical shift around 164.4 ppm as confirmed from the modeled 13C spectrum.

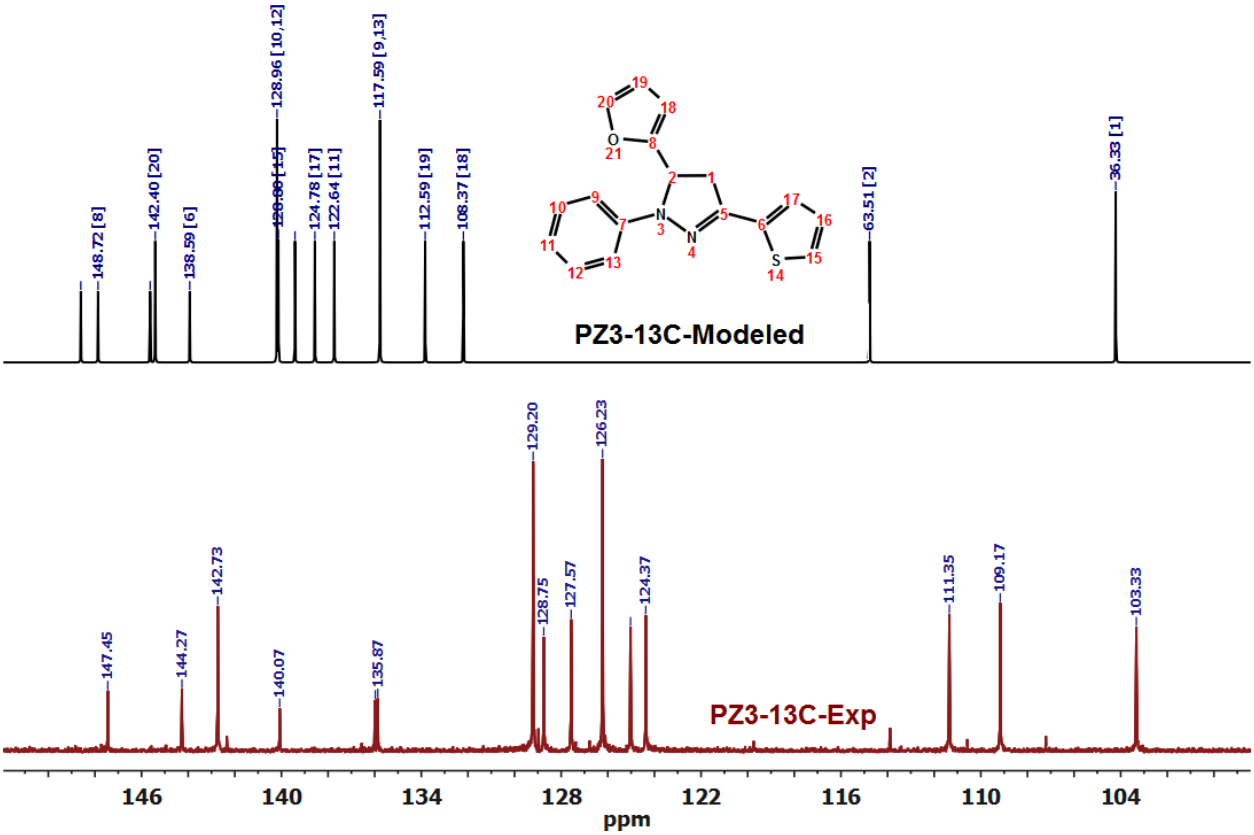

Figure S8. 13C NMR spectra for the modeled structure of 5-(furan-2-yl)-1-phenyl-3-(thiophen-2-yl)-4,5-dihydro-1H-pyrazole (PZ3) (black) and the corresponding experimental results (dark red) in deuterated chloroform ($CDCl_3$). The modeled results of 13C NMR (75 MHz, Common NMR Solvents) δ 150.63 (s), 148.72 (s), 142.96 (s), 142.40 (s), 138.59 (s), 128.88 (d, J = 11.5 Hz), 126.97 (s), 124.78 (s), 122.64 (s), 117.59 (s), 112.59 (s), 108.37 (s), 63.51 (s), 36.33 (s). The experimental 13C NMR spectrum of PZ3 shows that three peaks appear at 103.3, 109.2 and 147.5 ppm and assigned for pyarzole group. The furan group has four peaks at 111.4, 124.4, 140.1 and 144.3 ppm and 144.3 ppm, while the thiophene group has three peaks at 127.6, 128.8 and 136 ppm. The high intense peaks at 125, 126.2, 129.2 and 142.7 assigned to the carbons of the phenyl group.

FTIR data

All FTIR spectra in this study were collected using a Thermo Nicolet 6700 FTIR spectrometer (Thermo Scientific; 128 scans, 4 cm^{-1} resolution).

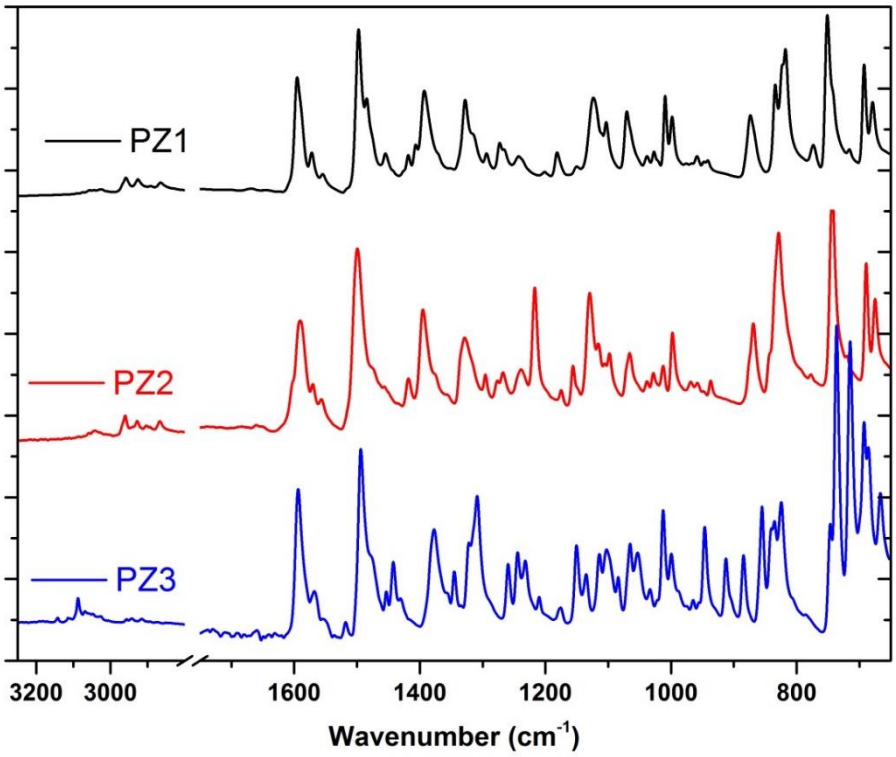

Figure S9. FTIR spectra for PZ1, PZ2 and PZ3. The spectra show that the PZ1 and PZ2 are similar, while PZ3 looks different because it has three different cyclic groups, which may have different vibration pattern. However, the three materials share three strong peaks around 750, 1500 and 1600 cm^{-1} which can assigned for the pyrazole group, which is the central core group in the three developed fluorophores.

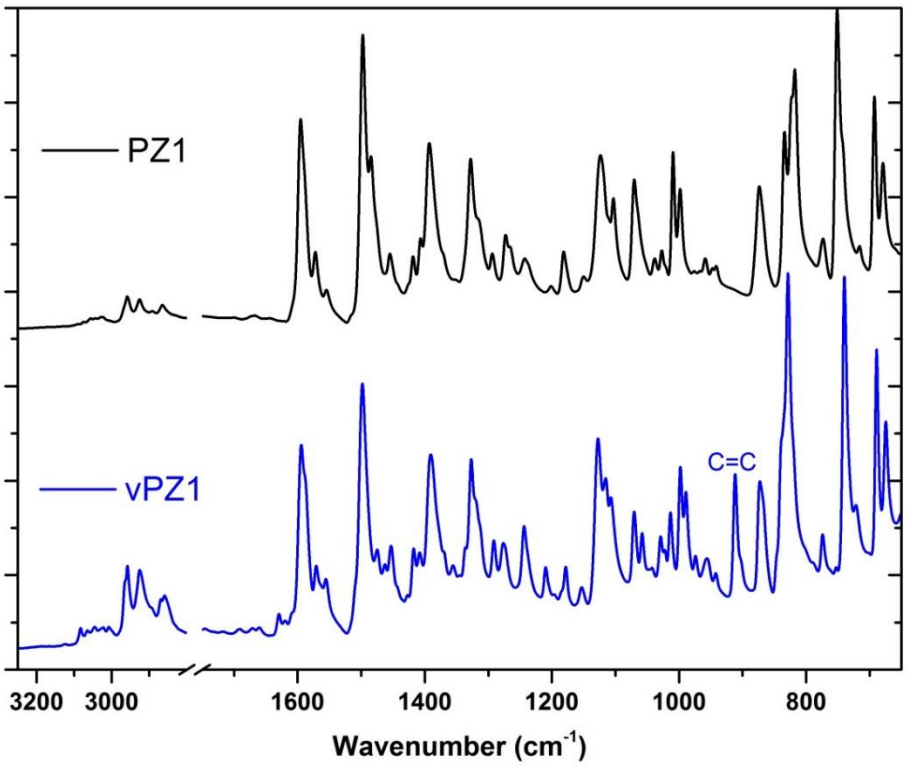

Figure S10. FTIR spectra for PZ1 and vPZ1. There are two new noticeable peaks at 911 cm^{-1} for vPZ1 and 1208 cm^{-1} that may be assigned to the C=C stretching of the added vinyl group.

The Procedure for Fluorescence Quantum Yield Measurements

Fluorescence quantum yield of a new fluorophore can be calculated relative to a standard sample with known Φ using equation [1, 2]:

$$\Phi_X = \Phi_{ST}\left(\frac{I_X}{Abs_X}\right)\left(\frac{Abs_{ST}}{I_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right)$$

Where the subscripts ST and X denote standard and test samples respectively, Φ is the fluorescence quantum yield, *I* is integrated intensity of the emission peak, *Abs* is absorbance of the solution, and η the refractive index of the solvent. If fluorophores are dissolved in the same solvent, the last term in the equation can be omitted. 2-(1-Naphthyl)-5-phenyloxazole (αNPO) and 9,10-Diphenylanthracene (DPA) standards were used for cross-calibration both having Φ values close to 100% [2,3].

All measurements were performed with the same equipment, using the same narrow slits and within the same day to avoid possible errors due to solvent evaporation of electronics drifts. The same diluted solutions, the same 10 mm path length quartz cuvettes, and the same solution volumes were used for optical fluorescence and absorbance measurements. Application of diluted solutions minimized influence of the self-absorption effect on the results. Excitation wavelength used in fluorescence measurements (shown in Table S1) corresponded to the position of the most red-shifted maximum in the absorption curve and simultaneously to the highest integrated fluorescence intensity of the emission in each case.

Table S1. Fluorescence intensity and absorptivity data for fluorophores under study in comparison to a standard DPA sample used for the fluorescence quantum yield calculation.

	0.0075 mM			0.015 mM			0.0225 mM				
Fluor	I, 10^7 [a.u.]	Abs	Φ^f [%]	I, 10^7 [a.u.]	Abs	Φ^f [%]	I, 10^7 [a.u.]	Abs	Φ^f [%]	λ [nm]	Φ^f_{aver} [%]
vPZ1	6.076	0.144	81.1	11.2	0.298	83.0	13.7	0.477	72.3	360	78.8
PZ1	9.694	0.146	128.1	14.7	0.293	110.6	20.5	0.474	108.9	360	115.9
PZ2	8.785	0.138	122.7	14.5	0.285	112.4	19.5	0.459	107.0	370	114.0
PZ3	8.092	0.134	116.8	14.2	0.268	116.9	19.3	0.429	113.3	380	115.6
DPA	5.887	0.114	100.0	10.2	0.225	100.0	14.3	0.36	100	375	100.0

cyclohexane solutions

	0.0075 mM			0.015 mM			0.0225 mM				
Fluor	I, 10^7 [a.u.]	Abs	Φ^f [%]	I, 10^7 [a.u.]	Abs	Φ^f [%]	I, 10^7 [a.u.]	Abs	Φ^f [%]	λ [nm]	Φ^f_{aver} [%]
vPZ1	5.800	0.120	72.6	9.431	0.228	76.5	12.1	0.382	73.7	360	74.3
PZ1	8.827	0.135	98.3	14.4	0.256	103.9	18.9	0.348	126.3	360	109.5
PZ2	9.453	0.132	107.6	15.8	0.277	105.3	20.6	0.449	106.7	360	106.6
PZ3	9.509	0.128	111.9	16.5	0.270	112.8	19.2	0.412	108.3	370	111.0

References:

[1] Williams, A. T. R.; Winfield, S. A.; Miller, J. N. Relative Fluorescence Quantum Yields Using a Computer Controlled Luminescence Spectrometer, *Analyst* **1983**, 108, 1067.

[2] Brouwer, A. M. Standards for Photoluminescence Quantum Yield Measurements in Solution (IUPAC Technical Report), *Pure Appl. Chem.* **2011**, 83 (12), 2213-2228.

[3] Seliman, A. F.; Bliznyuk, V. N.; Husson, S. M.; DeVol, T.A. Development of Polymerizable 2-(1-Naphthyl)-5-Phenyloxazole Scintillators for Ionizing Radiation Detection, *J. Mater. Chem. C* **2015**, 3 (27), 7053-7061.