# **Supporting Information**

# Design, synthesis of Donor-Acceptor pyrazabole derivatives for multiphoton absorption

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#### **Experimental section**

General Experimental. <sup>1</sup>H NMR (400 MHz), and <sup>13</sup>C NMR (100 MHz) spectra were recorded on Bruker Advance (III) 400 MHz. Chemical shifts in <sup>1</sup>H, and <sup>13</sup>C NMR spectra were reported in parts per million (ppm) with TMS (0 ppm), and CDCl<sub>3</sub> (77.23 ppm) as standards. UV-Visible absorption spectra of all the compounds in CH<sub>2</sub>Cl<sub>2</sub> were recorded on a Carry-100 Bio UV-visible Spectrophotometer. Electrochemical characterization of all the compounds was done by cyclic voltammetry. Cyclic voltammograms (CVs) were recorded on a CHI620D electrochemical analyzer using Platinum as working electrode, Platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. The scan rate was 100 mVS<sup>-1</sup>. A solution of tetrabutylammoniumhexafluorophosphate (TBAPF<sub>6</sub>) in  $CH_2Cl_2$  (0.1 M) was employed as the supporting electrolyte. CH<sub>2</sub>Cl<sub>2</sub> was freshly distilled from CaH<sub>2</sub> prior to use. The half-wave oxidation potential of ferrocene was measured to be 0.46 V against Ag/AgCl. Thermogravimetric analysis was done by using Mettler Toledo, TGA/DSC star<sup>e</sup> by using heating rate of 10 °C per HRMS was recorded on Brucker-Daltonics, Micro-TOF-Q II mass spectrometer. minute. Column chromatography was performed on Merck silica gel (230-400 mesh). All reagents were obtained from commercial sources.

The ns laser source is a frequency doubled Nd: YAG laser (INDI-40, Spectra-Physics) with a 6 ns pulse duration, and a repetition rate of 10 Hz at a 532 nm wavelength. The fs laser is a Spectra-Physics, Ti:Sapphire regenerative amplifier with 110 fs pulse duration and operated at 1 KHz repetition rate, and 800 nm wavelength. Ferrcocenyl substituted pyrazaboles are dissolved in  $CH_2Cl_2$  for the experimental studies. Open aperture Z-scan studies were carried out by focusing the input beam on to the sample using a lens of 120 mm focal length forming 27 µm and 40 µm spot sizes at the focus in ns, and fs regimes respectively. The transmitted light was

collected with a photodiode. The peak intensities,  $I_0$ , estimated at the focus in Z-scan experiments were approximately 0.7-1.5 GW/cm<sup>2</sup> in ns experiments, and approximately in the range of  $10^{12}$  W/cm<sup>2</sup> in fs experiments.

#### **Synthetic Procedure:**

#### Compound 2 -

Diiodopyrazabole **1** (0.2 g, 0.314 mmol), ferrocenylboronic acid (0.151 g, 0.659 mmol), CsF (0.095 g, 0.628 mmol), Ag<sub>2</sub>O (0.082 g, 0.345 mmol) were dissolved in dry THF (10.0 mL), and the solution was degassed with Argon. To this reaction mixture Pd(PPh<sub>3</sub>)<sub>4</sub> (0.036 g, 0.031 mmol) was added. After stirring at 80 °C for 24 h the solvent was removed under reduced pressure, and the residue subjected to column chromatography on silica (Hexane-DCM 93-7 in vol.) to yield the desired product **2** as red powder (0.108 g, 45.76%). Mp: 152 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  7.47 (s, 4H), 4.52 (s, 4H), 4.25 (s, 4H), 4.00 (m, 10H), 1.12-1.14 (m, 8H), 0.70-0.74 (m, 20H), 0.65 (m, 8H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  130.2, 120.4, 69.7, 68.4, 66.4, 27.8, 26.1, 14.2 ppm; HRMS (ESI): calcd. for C<sub>42</sub>H<sub>58</sub>B<sub>2</sub>Fe<sub>2</sub>N<sub>4</sub>: 752.3556 (*M*<sup>+</sup>), found 752.3572.

#### General procedure for compound 3, 4, 5 and 6 -

A solution of diiodopyrazabole **1** (0.314 mmol) in dry THF (4.0 mL) was prepared under Argon atmosphere, to this reaction mixture  $Pd(PPh_3)_2Cl_2$  (0.0157 mmol), CuI (0.0157 mmol), and Alkyne ferrocene (0.629 mmol) and diethylamine (1.5 mL) were added. The mixture was stirred for 24 h at 60 °C. After completion of the reaction, solvent was removed under vacuum, the crude product was purified by column chromatography.

#### Compound 3:

Reaction was carried out by general procedure and after completion of reaction product was purified by column chromatography (silica, Hexane-DCM 98-2 in vol.) to give the desired product **3** as a red powder (0.150 g, 60.0%). Mp: 206-208 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  7.72 (s, 4H), 4.52 (s, 4H), 4.2-4.3 (m, 14H), 1.20 (m, 8H), 0.80-0.83 (m, 20H), 0.70-0.59 (m, 8H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  135.8, 104.5, 89.8, 75.3, 71.2, 69.9, 68.8, 64.8, 27.4, 26.1, 14.0, 0.00 ppm; HRMS (ESI): calcd. for C<sub>46</sub>H<sub>58</sub>B<sub>2</sub>Fe<sub>2</sub>N<sub>4</sub>: 800.3558 (*M*<sup>+</sup>), found 800.3583.

#### **Compound 4:**

Reaction was carried by the general procedure, and after completion of reaction, product was purified by column chromatography (silica, Hexane-DCM 96-4 in vol.) to give the desired product **4** as a red powder (0.170 g, 56.85%). Mp: 216-220°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  7.79 (s, 4H), 7.47 (s, 8H), 4.70 (s, 4H), 4.38 (s, 4H), 4.07 (s, 10H), 1.22-1.24 (m, 8H), 0.81-0.84 (m, 20H), 0.74 (m, 8H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  140.1, 135.9, 131.4, 125.9, 119.9, 104.2, 91.4, 84.1, 79.2, 69.7, 69.4, 66.5, 27.4, 26.1, 14.0, 0.00 ppm; HRMS (ESI): calcd. for C<sub>58</sub>H<sub>66</sub>B<sub>2</sub>Fe<sub>2</sub>N<sub>4</sub>: 952.4187 (*M*<sup>+</sup>), found 952.4197.

#### **Compound 5:**

Reaction was carried by general procedure and after completion of reaction, product was purified by column chromatography (silica, Hexane-DCM 97-3 in vol.) to give the desired product **5** as a red powder (0.120 g, 40.26%). Mp: 205-207 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.84 (s, 4H), 7.68 (s, 2H), 7.49 (d, 2H, J=7.6 Hz), 7.39 (d, 2H, J=7.6 Hz), 7.31 (t, 2H, J=7.6 Hz), 4.71 (s, 4H), 4.38 (s, 4H), 4.05-4.10 (m, 10H), 1.23-1.28 (m, 8H), 0.73-0.77 (m, 8H), 0.83-0.87 (m, 20H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ 139.9, 136.1, 128.8, 128.7, 128.5, 126.2, 104.0,

84.1, 69.6, 69.2, 66.4, 27.4, 26.1, 14.0, 0.00 ppm; HRMS (ESI): calcd. for C<sub>58</sub>H<sub>66</sub>B<sub>2</sub>Fe<sub>2</sub>N<sub>4</sub>: 952.4187 (*M*<sup>+</sup>), found 952.4205.

#### **Compound 6:**

Reaction was carried by general procedure, and after completion of reaction, product was purified by column chromatography (silica, Hexane-DCM 97-3 in vol.) to give the desired product **6** as a red powder (0.170 g, 39%). Mp: 194-196 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  7.79 (s, 4H), 7.49 (s, 8H), 4.54 (s, 4H), 4.28 (s, 14H), 1.21-1.23 (m, 8H), 0.80-0.83 (m, 20H), 0.73 (m, 8H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  136.1, 131.4, 131.3, 128.7, 124.1, 121.9, 103.9, 91.1, 90.7, 85.4, 80.8, 71.5, 70.1, 69.0, 64.9, 53.4, 27.4, 26.1, 0.00 ppm; HRMS (ESI) calcd. for C<sub>62</sub>H<sub>66</sub>B<sub>2</sub>Fe<sub>2</sub>N<sub>4</sub>: 1000.4172 (*M*<sup>+</sup>), found 1000.4177.

## 1. X-ray crystallographic analysis

### **Crystallographic Details-**

The crystal structures of compound **3**, is shown in Figure S1. The important crystallographic parameters are listed in Table 1.

Table 1. Cry	stallographic dat	a and structure	refinement	detail for	compounds 3.
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Compound	3
Empirical formula	C <sub>23</sub> H <sub>29</sub> B Fe N <sub>2</sub>
Crystal size	0.33 x 0.26 x 0.21 mm
Crystal system Space group	Monoclinic P 21/c
Formula weight	400.14
<i>Т</i> ,К	293(2) K
Theta range for data collection	3.18 to 25.00 deg.

a ( Å)	13.8211(18)
b ( Å)	14.6473(9)
c ( Å)	11.4189(10)
A	90°
В	111.981(13)°
Г	90°
Z	4
F(000)	848
$V(A^{\circ})^{3}$	2143.6(4)
$D_{calc}$ , Mg m <sup>-3</sup>	1.240
Collected refins	16576
Unique refins	$3770 [R_{(int)} = 0.0667]$
Data/restrains/paramiters	3770 / 0 / 246
Final R indices $[I > 2\sigma(l)]^{6}$	R1 = 0.0987, wR2 = 0.2878
R indices (all data)	R1 = 0.1102, WR2 = 0.2992



Figure S1. Crystal structure of 3 (50% probability for thermal ellipsoids): Top view.

Crystallographic data reveals that compound are symmetric, the selected bond lengths, and bond angles of compound **3** is mentioned in Table 2.

Compound 3					
Bond lengt	hs (Å)	Bond angles $^{\circ}$			
B(1)-N(1)	1.571(8)	N(1)1-B(1)-N(2)	105.3(4)		
B(1)-N(2)	1.591(7)	N(1)1-B(1)-C(20)	111.0(5)		
B(1)-C(20)	1.598(10)	N(2)-B(1)-C(20)	111.0(5)		
B(1)-C(16)	1.619(10)	N(1)1-B(1)-C(16)	109.1(5)		
N(1)-C(1)	1.350(7)	N(2)-B(1)-C(16)	109.0(5)		
N(1)-N(2)	1.350(6)	C(20)-B(1)-C(16)	111.3(5)		
N(2)-C(3)	1.332(7)	C(1)-N(1)-N(2)	107.4(4)		
C(1)-C(2)	1.377(8)	N (2)-C (3)-C (2)	177.6 (7)		
C(2)-C(3)	1.380(9)	C(1)-N(1)-B(1)1	124.9(5)		
B(1)-B(1)	3.251	N(2)-N(1)-B(1)1	126.8(4)		

**Table 2.** Selected bond lengths, and bond angles of compound 3.

#### Multiphoton absorption properties:

Assuming a spatial and temporal Gaussian profile for laser pulses and utilizing the open aperture Z-scan theory for multi-photon absorption (MPA). We have the general equation for open aperture (OA) normalized energy transmittance given by

$$T_{OA(nPA)} = \frac{1}{\left[1 + (n-1)\alpha_n L(I_{00}/(1 + (z/z_0)^2))^{n-1}\right]^{\frac{1}{n-1}}}$$
(1)

where  $\alpha_n$  is the effective MPA coefficient (with n being the order or absorption process; n = 2 for 2PA; n = 3 for 3PA, and so on); I<sub>00</sub> is the peak intensity at the centre of the focus, z is the sample

position,  $z_0 = \frac{\pi \omega_0^2}{\lambda}$  is the Rayleigh range;  $\omega_0$  is the beam waist at the focal point (z = 0),  $\lambda$  is the laser wavelength; effective path lengths in the sample of length L for 2PA, 3PA is given as  $L_{eff} = \frac{1 - e^{-\alpha_0 L}}{\alpha_0}$ ,  $\dot{L}_{eff} = \frac{1 - e^{-2\alpha_0 L}}{2\alpha_0}$ . The two-photon and three-photon absorption cross sections can

be calculated by using the formulas  $\sigma_{TPA} = \frac{h\upsilon}{N}\alpha_2$  and  $\sigma_{3PA} = \frac{(h\upsilon)^2}{N}\alpha_3$  where N=N<sub>A</sub>D, where N

is the number of molecules per unit volume, *D* is the molar concentration of the compounds,  $N_A$  is the Avogadro constant, *h* is Planck's constant, and v is the frequency of laser beam used.

In order to assess the possible contribution of the solvent nonlinearity in ns regime, we conducted the OA Z-scan experiments on neat DCM at the same input intensities as the ones used with the sample. We observed that both the cuvette, and the solvent do not contribute to the signal in the ns regime. The closed aperture data,  $T_{CA}$ , are fitted to the equation

$$T_{CA} = 1 - \frac{4\Delta\phi(z/z_0)}{[1 + (z/z_0)^2][9 + (z/z_0)^2]}$$
(2)

Where  $\Delta \emptyset$  is the phase change of the laser beam due to nonlinear refraction.  $\Delta \emptyset$  value was estimated from the theoretical fits to experimental data. Nonlinear refractive index,  $n_2$  was calculated from

$$n_2(cm^2W^{-1}) = \frac{|\Delta\phi|\lambda}{2\pi I_{00}L_{eff}}$$
(3)

**Figure S3** shows the closed aperture Z-scan curves obtained for ferrocenyl substituted pyrazabole at peak intensities of  $0.16X10^{12}$  W/cm<sup>2</sup>, and  $0.28X10^{12}$  W/cm<sup>2</sup>. Open circles represent the experimental data while the solid lines are theoretical fit to the closed aperture scans using the equations [2] and [3]. Closed aperture Z scans were carried out at intensities, where the samples do not exhibit any nonlinear absorption, either 2PA or 3PA. Therefore the measured nonlinearities are not due to any resonant behaviour with the higher excited states. The closed aperture curves represent the normalized data. The curves were obtained at low peak intensities to avoid contributions to the nonlinearity that are also of non-electronic in origin. It is apparent that all of the samples, and DCM show negative nonlinearity as indicated by the peak-

valley structure. A ferrocenyl substituted pyrazabole derivative shows high nonlinear refraction while DCM shows lesser.









**Figure S2** shows the closed aperture *Z*-scan curves obtained for ferrocenyl substituted pyrazabole.

The nonlinear refractive index  $n_2$  values were calculated from the difference between normalized peak, and valley transmittance  $(\Delta T_{p-v})$  in the closed aperture Z-scan. The effective nonlinear refractive indices of the ferrocenyl substituted pyrazabole samples were calculated by subtracting the DCM contribution from the nonlinear refractive index values of the pyrazaboleferrocene-DCM solutions. We estimated the nonlinear refractive index at two different intensities  $(0.16X1012 \text{ W/cm}^2 \text{ and } 0.28X1012 \text{ W/cm}^2)$ , at which there is no 3PA, and the average value is shown in the Table 4. Table 4: Nonlinear refractive index values obtained at two different intensities for ferrocenyl substituted pyrazabole and average value has considered.

Compound	Average $n_2 (cm^2/W)$
2	-1.94 X10 <sup>-16</sup>
3	-3.42 X10 <sup>-16</sup>
4	-6.2 X10 <sup>-16</sup>
5	-6.1 X10 <sup>-16</sup>
6	-2.63 X10 <sup>-16</sup>
1	

#### Intensity dependant open aperture Z-scan results with ns laser:





0.7

-15

-10

-5





#### **Compound 6**

Figure S3: Intensity dependent open aperture Z-scan curves of compound 2, 3, 4, 5, 6 in ns regime.

These are the Open aperture Z-scan curves of pure DCM, and ferrocenyl substituted pyrazaboles at 800 nm, fs regime before removing the solvent contribution as followed our previous report Krishna et al.<sup>[1]</sup>





**Figure S5:** Open aperture Z-scan curves of pure DCM, and ferrocenyl substituted pyrazaboles at 800 nm, fs regime before removing the solvent contribution.

# Thermogravimetric analysis:





Figure S-6: TGA spectrum of compound 2.



3



Figure S-7: TGA spectrum of compound 3.





Figure S-8: TGA spectrum of compound 4.





Figure S-9: TGA spectrum of compound 6.



**Figure S-10**: <sup>1</sup>H-NMR spectrum of compound **2**.



**Figure S-11**: <sup>13</sup>C-NMR spectrum of compound **2**.





Figure S-12: HRMS spectrum of compound 2.



Figure S-13: <sup>1</sup>H-NMR spectrum of compound 3.



Figure S-14: <sup>13</sup>C-NMR spectrum of compound 3.







Figure S-15: HRMS spectrum of compound 3.



Figure S-16: <sup>1</sup>H-NMR spectrum of compound 4.



Figure S-17: <sup>13</sup>C-NMR spectrum of compound 4.



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Intens. x10 <sup>4</sup>	685.437 413.2671	4 952.4197					+MS, 0.1-0	.5min #(5-30)
0.5			1347.88	<sup>59</sup> 1637.8587	1927.8404			2880.3050
0.0	500	1000		1500	2000		2500	m/:
x10 <sup>4</sup>			952 4197				+MS, 0.1-0	.5min #(5-30
1.25			1					
1.00								
0.75		951 4229	9	53.4212				
0.50		1						
0.25	95	0.4243		954.424	7			
0.00	949.4241	1 /h	Jh	Jh A	955.4258		C58H66B2Fe2t	V4, M ,952.42
2000			952.4187					
1500			9	53.4202				
1000		951.4205 ∬		1				
500	949.4250	0.4215		954.423	955.4267			
04	948 950	95	52	954	956	~ ,	958	m/z
Bruker Compass	DataAnalysis 4.0		printed:	3/24/2012 5	5:41:39 PM		Page 1	of 1





Figure S-19: <sup>1</sup>H-NMR spectrum of compound 5.



**Figure S-20**: <sup>13</sup>C-NMR spectrum of compound **5**.



Figure S-21: HRMS spectrum of compound 5.



Figure S-22: <sup>1</sup>H-NMR spectrum of compound 6.



**Figure S-23**: <sup>13</sup>C-NMR spectrum of compound **6**.





Figure S-24: HRMS spectrum of compound 6.

# **References:**

(1) Murali Krishna M. B.; Venkatramaiah N.; Venkatesan R.; Rao D. N. J. Mater. Chem., **2012**, *22*, 3059-3068.