Supplementary material

Synthesis of pyrazole derivatives and their spectroscopic properties using both experimental and theoretical approaches

Adebayo A. Adeniyi and Peter A. Ajibade

Table S1: The four Ramsey terms of the N-N bonds in the ligands

			pz		
	FC	***SD***	***PSO***	***DSO***	***J***
*N1-N3	-5.220	-0.018	-1.197	0.022	-6.414
			bpzm		
N6-*N8	-5.492	-0.010	-1.215	0.029	-6.688
N9-*N10	-5.265	-0.017	-1.222	0.028	-6.476
***N8-*N10**	0.018	0.000	0.000	0.000	0.018
			bpza		
*N5-N9	-5.753	-0.023	-1.162	0.030	-6.908
*N6-N10	-5.753	-0.023	-1.162	0.030	-6.908
*N5-*N6	0.032	0.000	0.001	0.003	0.035
			bpzpya		
N10-*N14	-5.793	0.005	-1.150	0.030	-6.908
N12-*N15	-5.776	0.009	-1.129	0.030	-6.867
***N14-*N15**	0.009	0.001	-0.002	0.004	0.011
N_{py}-*N14	0.541	0.003	0.014	0.008	0.566
N_{py}-*N15	0.607	0.010	0.015	0.009	0.641

Table S2: The *N-N bond and H-bond properties of the ligands

					pz				
Bonds	GBL_I (au)	BPL - GBL_I	ρ(r)	$\nabla^2\rho(r)$	ε	V	G	∇^2Ven	V/G
*N1 - N3	2.560	1.06E-03	0.364	-0.680	0.131	-0.569	0.200	11.646	2.852
					bpzm				
N6 - *N8	2.569	7.63E-04	0.361	-0.659	0.130	-0.562	0.199	15.718	2.830
N9 - *N10	2.566	7.17E-04	0.362	-0.661	0.135	-0.566	0.200	15.541	2.826
					bpza				
*N5 - N9	2.578	5.87E-04	0.356	-0.640	0.129	-0.553	0.196	17.204	2.816
*N6 - N10	2.578	5.87E-04	0.356	-0.640	0.129	-0.553	0.196	17.204	2.816
#O12···H19	4.890	0.2281	0.009	0.035	0.756	-0.006	0.007	-0.693	0.810
#O12···H20	4.890	0.2280	0.009	0.035	0.755	-0.006	0.007	-0.693	0.810
					bpzpya				
N10 - *N14	2.580	8.35E-04	0.355	-0.635	0.112	-0.550	0.196	18.235	2.811
N12 - *N15	2.583	8.26E-04	0.354	-0.633	0.108	-0.548	0.195	18.161	2.812

The bonds with "#" represent the H-bonds while an atom with "*" represent the nitrogen atom on pyrazole that is available

for metal coordination.

Table S3: The QTAIM and NBO properties of the nitrogen atoms that are available (*N) and not available (N) for metal coordination.

Atom	q(A)	$\|\mu_{intra}(A)\|$	$\|\mu_{bond}(A)\|$	$\|\mu(A)\|$	Vol(A),0.001	$\chi_{Intra\_Iso}(A)$	$\chi_{bond\_Iso}(A)$	$\chi_{Iso}(A)$	$\chi_{zz}(A)$	$\sigma_{Iso}(A,A)$	$\sigma_{Iso}(A',A)$	$\sigma_{Iso}(A)$	Anisotropy	Occ	Energy
pz															
*N1	-0.68	0.78	0.95	1.16	119.03	-3.92	-4.44	-8.36	-15.79	-62.54	12.31	-50.23	352.31	1.94672	-0.39917
N3	-0.83	0.62	0.79	0.17	93.03	-4.41	-5.18	-9.60	-15.43	47.91	12.98	60.89	126.34	1.56142	-0.26347
Total	0.00	3.61	3.11	2.30	629.67	-20.31	-24.21	-44.51	-74.36	221.44	97.48	318.91	860.52		
bpzm															
N6	-0.828	0.578	0.814	0.282	70.337	-3.292	-5.747	-9.038	-7.925	29.574	13.470	43.044	136.58	1.55382	-0.27289
*N8	-0.682	0.767	0.974	1.129	116.792	-3.670	-4.313	-7.983	-5.944	-71.654	11.792	-59.862	336.50	1.9466	-0.40814
N9	-0.806	0.577	0.815	0.287	72.037	-3.231	-5.649	-8.880	-14.030	24.643	13.689	38.332	130.27	1.54606	-0.26187
*N10	-0.690	0.775	0.963	1.155	117.064	-3.801	-4.333	-8.135	-14.038	-67.342	12.001	-55.342	317.04	1.94645	-0.40211
Total	0.000	7.626	6.632	4.879	1293.130	-39.875	-51.939	-91.814	-106.811	499.094	203.463	702.557	1701.86		
bpza															
*N5	-0.687	0.765	0.986	1.133	116.402	-3.653	-4.274	-7.927	-5.486	-72.499	11.779	-60.720	304.82	1.94717	-0.40943
*N6	-0.687	0.765	0.985	1.133	116.399	-3.653	-4.275	-7.928	-5.487	-72.498	11.779	-60.719	304.82	1.94717	-0.40944
N9	-0.807	0.569	0.779	0.257	70.689	-3.270	-5.515	-8.785	-6.248	24.740	13.415	38.155	125.43	1.55934	-0.27117
N10	-0.807	0.569	0.779	0.257	70.606	-3.269	-5.516	-8.785	-6.249	24.742	13.416	38.158	125.43	1.55934	-0.27117
Total	0.000	9.101	10.499	7.032	1529.574	-51.928	-55.395	-107.322	-79.855	551.850	221.953	773.804	2412.24		
bpzpy															

*N_{py}	-1.112	0.054	0.944	0.907	109.016	-4.083	-4.337	-8.420	-16.473	-34.897	7.237	-27.660	436.16	1.89676	-0.35529
N10	-0.840	0.572	0.738	0.166	73.055	-3.150	-5.450	-8.599	-12.754	15.536	10.781	26.317	134.65	1.5341	-0.27632
N12	-0.841	0.571	0.738	0.170	73.513	-3.174	-5.269	-8.443	-13.371	16.260	10.557	26.818	131.58	1.53172	-0.27416
*N14	-0.653	0.766	1.003	1.062	112.748	-3.473	-4.180	-7.653	-12.722	-73.521	10.806	-62.715	349.89	1.94652	-0.40698
*N15	-0.656	0.768	1.013	1.061	112.415	-3.510	-4.096	-7.606	-13.655	-70.411	10.662	-59.749	352.41	1.94658	-0.40432
Total	0.000	10.396	12.224	8.071	1989.531	-63.173	-78.125	-141.298	-221.200	649.805	273.183	922.988	3638.08		

Table S4: The electronic excitation of the ligands showing their triplet and singlet transitions

Ligang	**State**	**Wavelength**	***f***	**Transitions**
pz	Triplet-A	290.64	0	H-1→L+1 (16%); HOMO→L+1 (104%); H-1→L+4 (7%); HOMO→L+9 (2%)
	Triplet-A	244.49	0	H-1→L+1 (94%); HOMO→L+1 (15%); HOMO→L+4 (3%);
	Triplet-A	211.04	0	H-2→L+1 (95%); H-2→L+4 (8%); HOMO→LUMO (3%);
	Singlet-A	207.98	0.0071	HOMO→LUMO (99%);
	Singlet-A	206.79	0	H-1→LUMO (93%);
	Singlet-A	205.26	0.0551	H-1→L+1 (40%); HOMO→L+1 (29%); HOMO→L+4 (11%); H-1→L+4 (3%)
bpzm	Triplet-A	297.73	0	H-2→LUMO (60%); H-2→L+1 (24%); H-1→LUMO (19%); H-3→LUMO (8%)
	Triplet-A	296.03	0	H-1→L+1 (12%); HOMO→LUMO (17%); HOMO→L+1 (42%); HOMO→L+2 (22%)
	Triplet-A	257.18	0	H-1→LUMO (14%); H-1→L+1 (35%); H-1→L+2 (15%); HOMO→L+1 (14%)
	Singlet-A	255.04	0.0024	HOMO→LUMO (75%); HOMO→L+1 (8%);
	Singlet-A	214.20	0.0592	H-1→LUMO (90%); H-2→LUMO (3%);
	Singlet-A	214.03	0.0073	H-2→LUMO (11%); H-1→L+1 (76%);
bpzcooh	Triplet-A	307.69	0	H-1→LUMO (18%); H-1→L+3 (19%); HOMO→L+1 (47%); HOMO→L+2 (10%)
	Triplet-A	307.03	0	H-1→L+1 (32%); HOMO→LUMO (28%); HOMO→L+3 (24%); H-3→L+1 (7%)
	Triplet-A	265.21	0	H-6→LUMO (14%); H-3→LUMO (40%); H-2→L+1 (20%); H-

				1→LUMO (19%)
	Singlet-A	264.41	0.001	HOMO→LUMO (93%);
	Singlet-A	253.16	0.0145	H-1→LUMO (87%) H-6→LUMO (3%); H-3→LUMO (4%);
	Singlet-A	248.42	0.0342	H-2→LUMO (94%);
bpzpya	Triplet-A	406.98	0	HOMO→LUMO (104%); H-8→LUMO (2%);
	Triplet-A	386.82	0	H-3→LUMO (10%); HOMO→L+1 (82%); H-9→LUMO (7%); H-9→L+1 (3%)
	Triplet-A	349.08	0	H-1→LUMO (40%); H-1→L+1 (32%); H-1→L+2 (15%); H-2→L+1 (4%)
	Singlet-A	338.64	0.1315	HOMO→LUMO (88%);
	Singlet-A	334.79	0.001	H-1→LUMO (88%);
	Singlet-A	322.55	0.0012	H-2→LUMO (89%); H-3→LUMO (3%); ;

Table S5: The molecular orbital (MO) contribution of the nitrogen atom(s) "*N" available for metal coordination and nitrogen atom "N" in pz not available for metal coordination.

pz

MO	eV	*N1	N3	others
L+5	1.41	-39	10	130
L+4	1.18	-4	0	106
L+3	0.82	71	-86	116
L+2	0.67	-18	15	105
L+1	-0.02	26	14	60
LUMO	-0.05	-54	-23	179
HOMO	-6.98	32	1	66
H-1	-7.26	7	32	61
H-2	-8.18	77	4	19
H-3	-11.03	3	2	95
H-4	-11.83	7	10	82
H-5	-12	23	45	33
H-6	-12.24	13	16	71
H-7	-14.97	10	12	77

bpzm

MO	eV	*N8	*N10	others
L+5	0.69	37	9	55
L+4	0.51	-6	1	106
L+3	0.46	-4	-19	125
L+2	0.07	-41	-9	152
L+1	-0.37	2	6	93
LUMO	-0.54	18	4	78
HOMO	-7	0	29	71
H-1	-7.05	5	6	89
H-2	-7.33	28	2	70
H-3	-7.5	5	2	93
H-4	-8.25	2	73	25
H-5	-8.42	73	2	25
H-6	-10.89	2	6	92
H-7	-11.03	2	3	95

bpza

MO	eV	*N5	*N6	others
L+5	0.47	-22	-21	145

L+4	0.25	-23	-23	148	
L+3	0.15	13	13	75	
L+2	-0.37	-6	-6	114	
L+1	-0.71	8	8	84	
LUMO	-1.45	1	1	99	
HOMO	-7.11	17	16	67	
H-1	-7.26	12	15	73	
H-2	-7.27	4	2	95	
H-3	-7.58	7	7	87	
H-4	-8.38	37	34	29	
H-5	-8.48	36	39	25	
H-6	-8.92	2	2	97	
H-7	-9.9	0	0	100	

bpzpya

MO	eV	*N9	*N15	*N14	others
L+5	0.23	2	2	-32	129
L+4	0.05	-6	-48	4	153
L+3	-0.83	0	4	-3	100
L+2	-0.86	4	5	-5	97
L+1	-2.01	1	3	4	92
LUMO	-2.66	16	0	0	85
HOMO	-6.93	0	0	0	100
H-1	-7.31	2	28	1	69
H-2	-7.39	1	3	29	67
H-3	-7.54	11	5	6	77
H-4	-7.99	36	26	12	25
H-5	-8.37	1	28	47	25
H-6	-8.41	3	3	0	94
H-7	-8.78	35	19	18	28

Table S6: Correlation of molecular properties (bold italic) of the ligands to the atomic properties of *N and its bond *N-N (bold) and *N···*N (bold). The most highly correlated values are in bold.

	^{15}*N-NMR shift	*N···*N J-coupling	**J**	Bond-length	Bond-strain	$\nabla^2\rho(r)$	Γ	ß	LUMO	Band-Gap
*N-NMR shift	1.00	0.55	**-0.95**	**0.93**	-0.77	**0.94**	**0.91**	0.62	-0.80	-0.78
J-coupling (*N···*N)	0.55	1.00	-0.55	0.64	0.04	0.64	0.19	**1.00**	**-0.88**	**-0.91**
FC	**-0.93**	-0.61	**1.00**	**-1.00**	0.76	**-1.00**	-0.77	-0.68	**0.90**	**0.88**
SD	0.49	**0.89**	-0.33	0.41	0.18	0.42	0.22	**0.87**	-0.66	-0.70
PSO	0.51	0.71	-0.72	0.79	-0.33	0.78	0.19	0.74	**-0.87**	**-0.86**
DSO	**0.99**	0.43	**-0.94**	**0.91**	**-0.86**	**0.92**	**0.95**	0.50	-0.73	-0.70
J	**-0.95**	-0.55	1.00	**-0.99**	0.81	**-0.99**	-0.81	-0.62	**0.86**	0.83
Bond-length	**0.93**	0.64	**-0.99**	1.00	-0.74	**1.00**	0.75	0.70	**-0.92**	**-0.89**
Bond-strain	-0.77	0.04	0.81	-0.74	1.00	-0.74	**-0.88**	-0.05	0.41	0.36

$\rho(r)$	**-0.88**	-0.66	**0.97**	**-0.99**	0.69	**-0.99**	-0.67	-0.72	**0.94**	**0.91**
$\nabla^2\rho(r)$	**0.94**	0.64	**-0.99**	**1.00**	-0.74	1.00	0.76	0.70	**-0.92**	**-0.89**
ε	-0.59	**-1.00**	0.58	-0.67	0.01	-0.67	-0.22	**-1.00**	**0.90**	**0.93**
V	**0.90**	0.69	**-0.98**	**1.00**	-0.68	**0.99**	0.69	0.75	**-0.95**	**-0.93**
G	-0.82	-0.60	**0.96**	**-0.97**	0.70	**-0.97**	-0.61	-0.66	**0.90**	**0.87**
∇^2Ven	**0.98**	0.62	**-0.98**	**0.98**	-0.76	**0.98**	0.85	0.68	**-0.88**	**-0.86**
|V/G|	**-0.96**	-0.63	**0.99**	**-0.99**	0.76	**-1.00**	-0.80	-0.69	**0.90**	**0.88**
q(A)	0.38	**0.97**	-0.34	0.44	0.26	0.44	0.02	**0.95**	-0.75	-0.79
$\lvert\mu_{intra}(A)\rvert$	**-0.98**	-0.37	**0.94**	**-0.89**	**0.88**	**-0.90**	**-0.97**	-0.44	0.69	0.66
$\lvert\mu_{bond}(A)\rvert$	**0.94**	0.77	**-0.95**	**0.97**	-0.61	**0.98**	0.72	**0.82**	**-0.96**	**-0.95**
$\lvert\mu(A)\rvert$	-0.77	**-0.96**	0.72	-0.78	0.21	-0.78	-0.47	**-0.97**	**0.93**	**0.95**
Vol(A)	**-0.84**	**-0.91**	0.82	**-0.87**	0.36	**-0.87**	-0.56	**-0.94**	**0.96**	**0.97**
$\chi_{Intra\_Iso}(A)$	**0.96**	0.77	**-0.91**	**0.92**	-0.57	0.93	0.76	0.82	**-0.92**	**-0.91**
$\chi_{bond\_Iso}(A)$	**0.95**	0.78	**-0.93**	**0.95**	-0.59	**0.96**	0.73	0.83	**-0.95**	**-0.94**
$\chi_{Iso}(A)$	**0.95**	0.78	**-0.92**	**0.94**	-0.58	**0.94**	0.75	0.83	**-0.93**	**-0.92**
$\chi_{zz}(A)$	0.61	-0.32	-0.55	0.45	**-0.91**	0.45	0.87	-0.24	-0.07	-0.02
$\sigma_{Iso}(A,A)$	**-1.00**	-0.49	**0.94**	**-0.92**	0.81	**-0.92**	**-0.94**	-0.56	0.76	0.74
$\sigma_{Iso}(A',A)$	-0.81	**-0.93**	0.77	-0.83	0.29	-0.83	-0.52	**-0.96**	**0.95**	**0.96**
$\sigma_{Iso}(A)$	**-1.00**	-0.55	**0.95**	**-0.93**	0.77	**-0.94**	**-0.91**	-0.62	0.80	0.78
Anisotropy	-0.40	0.39	0.54	-0.45	**0.88**	-0.45	-0.58	0.31	0.09	0.03
Occupation	0.00	-0.50	-0.24	0.19	-0.59	0.17	0.14	-0.45	0.09	0.16
Energy	**-0.92**	-0.19	**0.88**	-0.82	**0.94**	-0.82	**-0.98**	-0.27	0.55	0.52
Dipole	0.70	0.30	-0.43	0.39	-0.38	0.41	0.77	0.32	-0.30	-0.32
$\Sigma_i\langle\alpha\rangle_i$										
	0.89	**0.87**	**-0.88**	**0.92**	-0.46	**0.92**	0.63	**0.91**	**-0.97**	-0.97
Δα1	-0.36	**-0.98**	0.37	-0.48	-0.23	-0.48	0.03	**-0.96**	0.79	0.82
Δα2	0.58	**0.99**	-0.52	0.60	0.04	0.61	0.24	**0.98**	**-0.84**	**-0.88**
Δα3	0.55	**1.00**	-0.52	0.60	0.06	0.61	0.20	**0.99**	**-0.86**	**-0.89**
Γ	**0.91**	0.19	-0.81	0.75	-0.88	0.76	**1.00**	0.26	-0.49	-0.47
β	0.62	**1.00**	-0.62	0.70	-0.05	0.70	0.26	1.00	**-0.92**	**-0.94**
HOMO	-0.10	0.62	0.26	-0.17	0.70	-0.16	-0.33	0.56	-0.18	-0.25
LUMO	-0.80	**-0.88**	**0.86**	**-0.92**	0.41	**-0.92**	-0.49	**-0.92**	**1.00**	**1.00**
Band-Gap	-0.78	**-0.91**	**0.83**	**-0.89**	0.36	**-0.89**	-0.47	**-0.94**	1.00	1.00
Non-Lewis orbital	-0.02	0.77	0.10	0.00	0.64	0.01	-0.34	0.72	-0.39	-0.44