Electronic Supplementary Information

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Title: B–H_b···π interaction in borane-graphene complexes: Coronene as a case study

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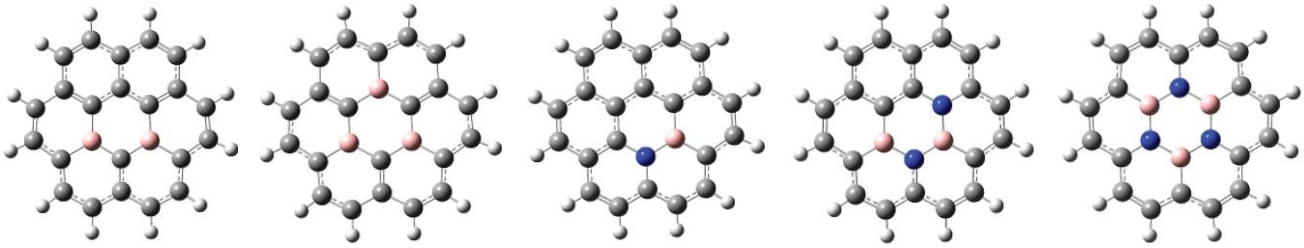
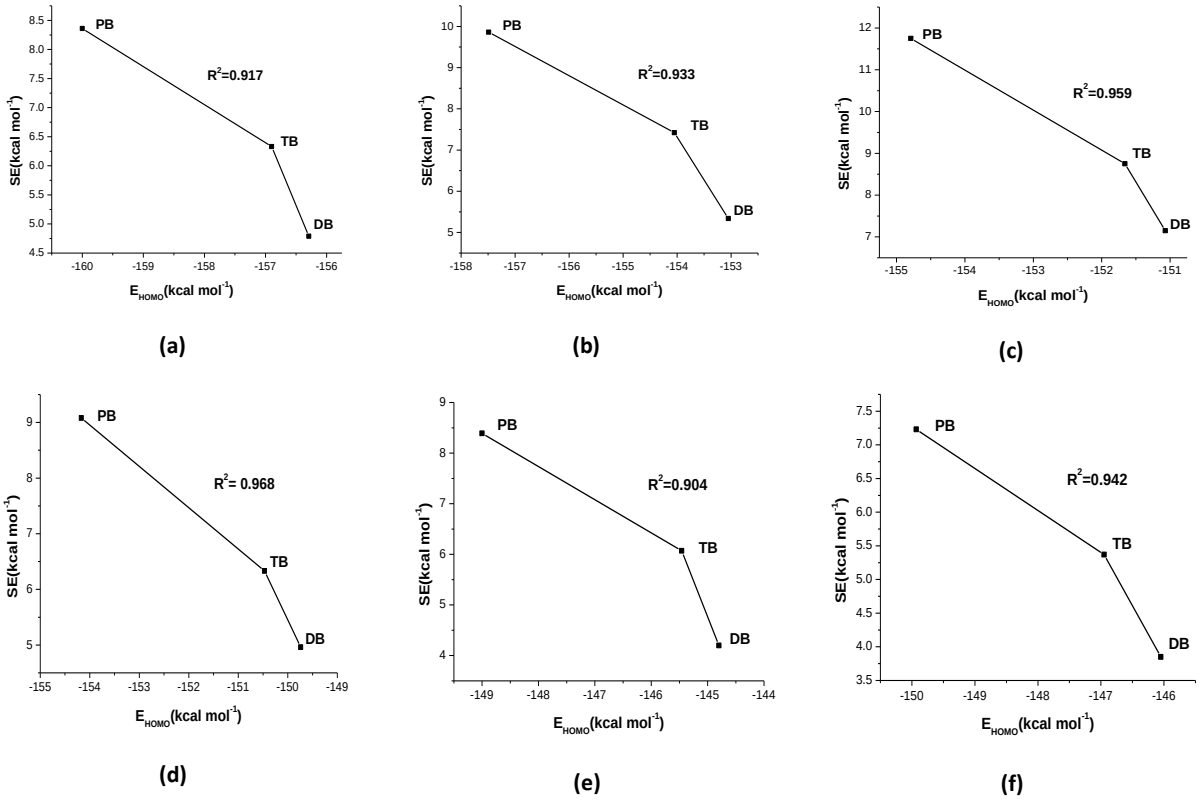
(a) Charge=0 Multiplicity=1 E^C =-578290.7 | (b) Charge=0 Multiplicity=2 E^C =-588692.9 | (c) Charge=0 Multiplicity=1 E^C =-599091.2 | (d) Charge=0 Multiplicity=2 E^C =-609489.0 | (e) Charge=0 Multiplicity=2 E^C =-569942.9

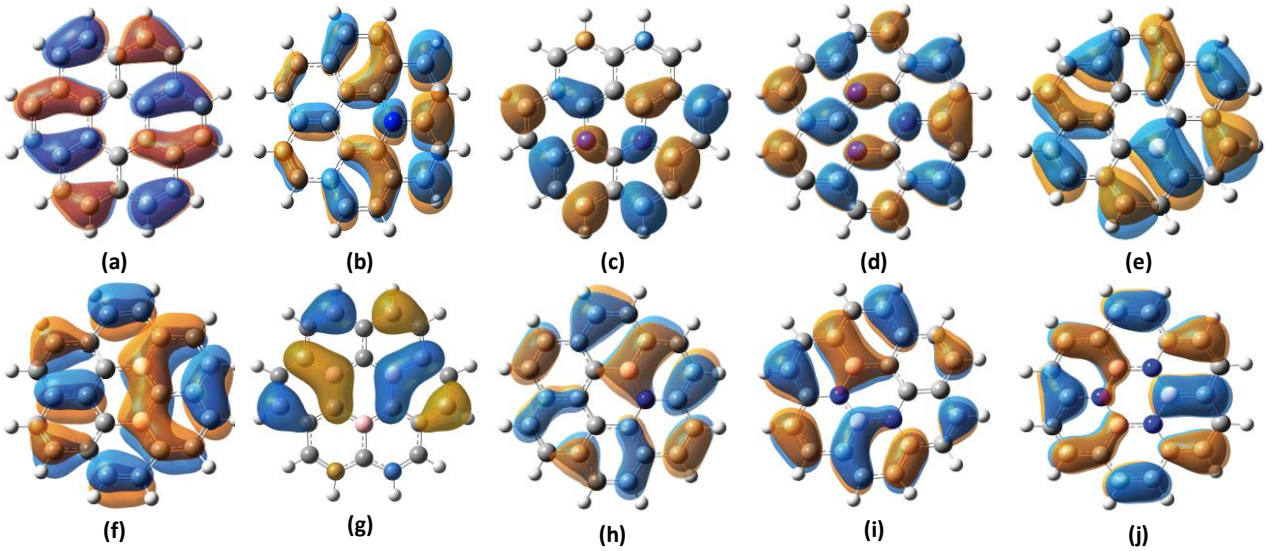


(f) Charge=0 Multiplicity=1 E^C =-561587.3 | (g) Charge=0 Multiplicity=2 E^C =-553239.0 | (h) Charge=0 Multiplicity=1 E^C =-580428.2 | (i) Charge=0 Multiplicity=1 E^C =-582595.7 | (j) Charge=0 Multiplicity=1 E^C =-584790.2

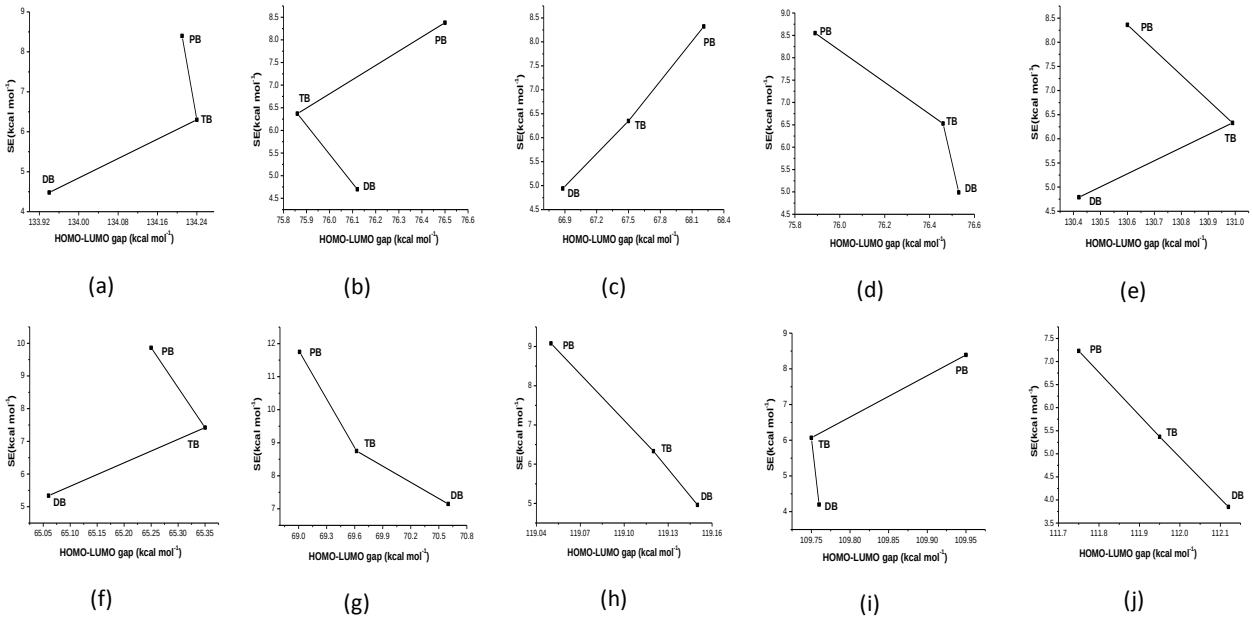
Supplementary Fig. S1 Gas phase optimized structures with their respective charge, multiplicity and energy (kcal mol^{-1}) for (a) Cor (b) $Cor_{(N)}$ (c) $Cor_{(2N)}$ (d) $Cor_{(3N)}$ (e) $Cor_{(B)}$ (f) $Cor_{(2B)}$ (g) $Cor_{(3B)}$ (h) $Cor_{(BN)}$ (i) $Cor_{(2BN)}$ (j) $Cor_{(3BN)}$ obtained at M06-2X/6-31++G(d,p) level of theory.



Supplementary Fig. S2 Plot of E_{HOMO} vs SE with R^2 values for the complexes formed by (a) $Cor_{(B)}$ (b) $Cor_{(2B)}$ (c) $Cor_{(3B)}$ (d) $Cor_{(BN)}$ (e) $Cor_{(2BN)}$ (f) $Cor_{(3BN)}$ obtained at M06-2X/6-31++G(d,p) level of theory.



Supplementary Fig. S3 Shapes of E_{HOMO} for (a) Cor (b) $Cor_{(N)}$ (c) $Cor_{(2N)}$ (d) $Cor_{(3N)}$ (e) $Cor_{(B)}$ (f) $Cor_{(2B)}$ (g) $Cor_{(3B)}$ (h) $Cor_{(BN)}$ (i) $Cor_{(2BN)}$ (j) $Cor_{(3BN)}$ obtained at M06-2X/6-31++G(d,p) level of theory.



Supplementary Fig. S4 Plot of ΔE vs SE for the complexes formed by (a) Cor (b) $Cor_{(N)}$ (c) $Cor_{(2N)}$ (d) $Cor_{(3N)}$ (e) $Cor_{(B)}$ (f) $Cor_{(2B)}$ (g) $Cor_{(3B)}$ (h) $Cor_{(BN)}$ (i) $Cor_{(2BN)}$ (j) $Cor_{(3BN)}$ obtained at M06-2X/6-31++G(d,p) level of theory.

Supplementary Table S1 NPA charge (NBO analysis) for free boranes and their complexes obtained at M06-2X/6-31++G(d,p) level of theory.

System/ Complex	Charge, q at H_b	Charge Transfer, Δq	System/ Complex	Charge, q at H_b	Charge Transfer, Δq	System/ Complex	Charge, q at H_b	Charge Transfer, Δq
DB	0.114	-	TB	0.200	-	PB	0.173	-
Cor···DB	0.104	0.010	Cor···TB	0.197	0.003	Cor···PB	0.169	0.004
$Cor_{(N)}$···DB	0.098	0.016	$Cor_{(N)}$···TB	0.192	0.008	$Cor_{(N)}$···PB	0.164	0.009
$Cor_{(2N)}$···DB	0.097	0.017	$Cor_{(2N)}$···TB	0.181	0.019	$Cor_{(2N)}$···PB	0.153	0.020
$Cor_{(3N)}$···DB	0.094	0.020	$Cor_{(3N)}$···TB	0.177	0.023	$Cor_{(3N)}$···PB	0.150	0.023
$Cor_{(B)}$···DB	0.108	0.007	$Cor_{(B)}$···TB	0.201	–0.001	$Cor_{(B)}$···PB	0.173	0.000
$Cor_{(2B)}$···DB	0.114	0.000	$Cor_{(2B)}$···TB	0.206	–0.006	$Cor_{(2B)}$···PB	0.180	–0.007
$Cor_{(3B)}$···DB	0.110	0.004	$Cor_{(3B)}$···TB	0.206	–0.006	$Cor_{(3B)}$···PB	0.175	–0.002
$Cor_{(BN)}$···DB	0.107	0.007	$Cor_{(BN)}$···TB	0.197	0.002	$Cor_{(BN)}$···PB	0.166	0.007
$Cor_{(2BN)}$···DB	0.097	0.017	$Cor_{(2BN)}$···TB	0.195	0.005	$Cor_{(2BN)}$···PB	0.163	0.010
$Cor_{(3BN)}$···DB	0.096	0.018	$Cor_{(3BN)}$···TB	0.186	0.014	$Cor_{(3BN)}$···PB	0.158	0.015

Supplementary Table S2 The B-H_b distance (in Å) in free borane and in their complexes obtained at M06-2X/6-31++G(d,p) level of theory

System/complex	B-H_b distance	System/complex	B-H_b distance	B-H_b distance	System/complex	B-H_b distance
DB	1.3128	TB	1.2517	1.4112	PB	1.3419
Cor···DB	1.3089	Cor···TB	1.2543	1.4129	Cor···PB	1.3411
$Cor_{(N)}$···DB	1.3067	$Cor_{(N)}$···TB	1.2540	1.4124	$Cor_{(N)}$···PB	1.3393
$Cor_{(2N)}$···DB	1.3121	$Cor_{(2N)}$···TB	1.2541	1.4188	$Cor_{(2N)}$···PB	1.3390
$Cor_{(3N)}$···DB	1.3118	$Cor_{(3N)}$···TB	1.2534	1.4149	$Cor_{(3N)}$···PB	1.3387
$Cor_{(B)}$···DB	1.3070	$Cor_{(B)}$···TB	1.2545	1.4195	$Cor_{(B)}$···PB	1.3392
$Cor_{(2B)}$···DB	1.3061	$Cor_{(2B)}$···TB	1.2549	1.4135	$Cor_{(2B)}$···PB	1.3396
$Cor_{(3B)}$···DB	1.3089	$Cor_{(3B)}$···TB	1.2545	1.4126	$Cor_{(3B)}$···PB	1.3403
$Cor_{(BN)}$···DB	1.3111	$Cor_{(BN)}$···TB	1.2546	1.4128	$Cor_{(BN)}$···PB	1.3396
$Cor_{(2BN)}$···DB	1.3078	$Cor_{(2BN)}$···TB	1.2540	1.4121	$Cor_{(2BN)}$···PB	1.3357
$Cor_{(3BN)}$···DB	1.3108	$Cor_{(3BN)}$···TB	1.2525	1.4142	$Cor_{(3BN)}$···PB	1.3387

Supplementary Table S3 E_{HOMO}, E_{LUMO} and ΔE (in kcal mol^{-1}) of undoped/doped Cor and their respective complexes in cyclohexane (ch) and water (wat) obtained at M06-2X/6-31++G(d,p) level of theory.

Systems	$E_{HOMO(ch)}$	$E_{LUMO(ch)}$	$\Delta E_{(ch)}$	$E_{HOMO(wat)}$	$E_{LUMO(wat)}$	$\Delta E_{(wat)}$
Cor	−158.23	−23.61	134.62	−160.99	−26.56	134.43
$Cor_{(N)}$	−98.47	−22.36	76.11	−100.92	−24.60	76.32
$Cor_{(2N)}$	−95.02	−27.67	67.35	−97.43	−29.58	67.85
$Cor_{(3N)}$	−98.36	−21.41	76.95	−100.26	−23.27	76.99
$Cor_{(B)}$	−156.19	−24.60	131.58	−158.71	−27.32	131.39
$Cor_{(2B)}$	−153.19	−88.49	64.71	−158.18	−91.30	66.88
$Cor_{(3B)}$	−151.30	−81.48	69.82	−154.33	−84.51	69.82
$Cor_{(BN)}$	−149.81	−30.38	119.43	−152.69	−32.81	119.89
$Cor_{(2BN)}$	−144.84	−34.65	110.18	−147.63	−36.72	110.82
$Cor_{(3BN)}$	−146.08	−33.84	112.24	−148.23	−35.84	112.38
Cor···DB	−158.79	−24.81	133.98	−161.53	−27.43	134.10
Cor···TB	−159.35	−25.08	134.27	−161.53	−27.14	134.39
Cor···PB	−161.83	−27.57	134.26	−162.59	−28.22	134.37
$Cor_{(N)}$···DB	−99.37	−23.14	76.23	−102.03	−25.60	76.43
$Cor_{(N)}$···TB	−99.74	−23.78	75.96	−101.86	−25.73	76.13
$Cor_{(N)}$···PB	−102.89	−26.29	76.60	−103.57	−26.83	76.74
$Cor_{(2N)}$···DB	−95.61	−28.44	67.17	−98.32	−30.60	67.72
$Cor_{(2N)}$···TB	−96.64	−28.90	67.74	−99.00	−30.83	68.17
$Cor_{(2N)}$···PB	−99.68	−31.26	68.42	−100.43	−31.74	68.69
$Cor_{(3N)}$···DB	−99.46	−22.84	76.62	−101.76	−25.04	76.72
$Cor_{(3N)}$···TB	−99.75	−23.25	76.50	−101.77	−25.21	76.56
$Cor_{(3N)}$···PB	−102.16	−26.26	75.90	−102.67	−26.71	75.96
$Cor_{(B)}$···DB	−156.86	−26.55	130.32	−159.46	−29.30	130.16
$Cor_{(B)}$···TB	−157.10	−26.16	130.94	−159.21	−28.42	130.79
$Cor_{(B)}$···PB	−159.37	−28.86	130.52	−160.11	−29.61	130.51
$Cor_{(2B)}$···DB	−153.89	−88.52	65.37	−157.15	−91.11	66.04
$Cor_{(2B)}$···TB	−154.53	−88.89	65.64	−157.18	−90.88	66.30
$Cor_{(2B)}$···PB	−157.24	−91.70	65.53	−158.45	−92.26	66.20
$Cor_{(3B)}$···DB	−151.80	−81.19	70.61	−154.47	−83.89	70.58
$Cor_{(3B)}$···TB	−152.06	−82.41	69.65	−154.38	−84.64	69.74
$Cor_{(3B)}$···PB	−154.47	−85.44	69.03	−155.32	−86.19	69.13
$Cor_{(BN)}$···DB	−150.45	−31.10	119.35	−153.45	−33.67	119.77
$Cor_{(BN)}$···TB	−150.94	−31.61	119.33	−153.50	−33.76	119.74
$Cor_{(BN)}$···PB	−153.74	−34.49	119.25	−154.53	−34.85	119.58
$Cor_{(2BN)}$···DB	−145.54	−35.44	110.1	−148.56	−37.76	110.80
$Cor_{(2BN)}$···TB	−145.92	−35.89	110.08	−148.52	−37.71	110.81
$Cor_{(2BN)}$···PB	−148.59	−38.32	110.28	−149.48	−38.59	110.89
$Cor_{(3BN)}$···DB	−146.59	−34.40	112.19	−149.02	−36.68	112.34
$Cor_{(3BN)}$···TB	−147.20	−35.18	112.02	−149.18	−36.97	112.21
$Cor_{(3BN)}$···PB	−149.42	−37.60	111.82	−150.02	−37.98	112.04

Supplementary Table S4 BSSE correction (in kcal mol^{-1}) for the complexes of undoped/doped Cor with boranes obtained at M06-2X/6-31++G(d,p) level of theory.

complex	BSSE correction	complex	BSSE correction	complex	BSSE correction
Cor···DB	0.81	-	-	-	-
Cor···TB	1.10	-	-	-	-
Cor···PB	1.38	-	-	-	-
$Cor_{(N)}$···DB	0.80	$Cor_{(B)}$···DB	0.68	$Cor_{(BN)}$···DB	0.71
$Cor_{(N)}$···TB	1.07	$Cor_{(B)}$···TB	0.91	$Cor_{(BN)}$···TB	0.95
$Cor_{(N)}$···PB	1.36	$Cor_{(B)}$···PB	1.22	$Cor_{(BN)}$···PB	1.28
$Cor_{(2N)}$···DB	0.86	$Cor_{(2B)}$···DB	0.72	$Cor_{(2BN)}$···DB	0.71
$Cor_{(2N)}$···TB	1.16	$Cor_{(2B)}$···TB	0.98	$Cor_{(2BN)}$···TB	0.93
$Cor_{(2N)}$···PB	1.48	$Cor_{(2B)}$···PB	1.37	$Cor_{(2BN)}$···PB	1.28
$Cor_{(3N)}$···DB	0.93	$Cor_{(3B)}$···DB	0.81	$Cor_{(3BN)}$···DB	0.67
$Cor_{(3N)}$···TB	1.21	$Cor_{(3B)}$···TB	1.00	$Cor_{(3BN)}$···TB	0.86
$Cor_{(3N)}$···PB	1.61	$Cor_{(3B)}$···PB	1.42	$Cor_{(3BN)}$···PB	1.16

Supplementary Table S5 λ_{max} values and their corresponding oscillator strength (*f*), excitation energy (E) with dominant transition for undoped/doped Cor in THF obtained at B3LYP/6-31++G(d,p) level of theory.

Systems	λ_{max} in nm	Oscillator strength, f	Excitation energy in eV	Dominant transition	Orbital contribution
Cor	307.6	0.985	4.03	HOMO-1→LUMO+1	0.465
				HOMO→LUMO	0.462
$Cor_{(N)}$	376.9	0.068	3.30	(HOMO-2)A→LUMOA	0.566
				(HOMO-2)B→HOMOB	0.496
	581.0	0.035	2.13	HOMOA→(LUMO+3)A	0.972
				(HOMO-2)B→LUMOB	0.131
$Cor_{(2N)}$	352.2	0.055	3.52	HOMO-2→LUMO	0.583
				HOMO-1→LUMO+1	0.375
	542.4	0.140	2.29	HOMO→LUMO+3	0.684
$Cor_{(3N)}$	579.9	0.181	2.14	HOMOA→(LUMO+2)A	0.588
				(HOMO-1)B→ (LUMO+2)B	0.768
$Cor_{(B)}$	329.7	0.134	3.76	(HOMO-1)A→(LUMO+1)A	0.531
				(HOMO-1)B→LUMOB	0.531
	503.7	0.046	2.46	(HOMO-1)A→LUMO A	0.240
				(HOMO-5)B→LUMO B	0.911
$Cor_{(2B)}$	300.7	0.582	4.12	HOMO-2→LUMO+1	0.347
				HOMO-1→LUMO+2	0.418
	495.5	0.145	2.50	HOMO-4→LUMO	0.677
				HOMO→LUMO+1	0.108
$Cor_{(3B)}$	573.2	0.207	2.16	(HOMO-3)A→LUMO A	0.796
				(HOMO-3)B→HOMOB	0.571
$Cor_{(BN)}$	250.8	0.248	4.94	HOMO-1→LUMO+1	0.289
				HOMO→LUMO+2	0.500
	327.9	0.530	3.78	HOMO-3→LUMO	0.517
				HOMO-2→LUMO+2	0.309
$Cor_{(2BN)}$	274.9	0.204	4.51	HOMO-1→LUMO+1	0.144
				HOMO→LUMO	0.634
	345.2	0.580	3.59	HOMO-3→LUMO	0.606
				HOMO→LUMO+3	0.235
$Cor_{(3BN)}$	272.7	0.083	4.55	HOMO-1→LUMO	0.351
				HOMO→LUMO+1	0.344
	357.9	1.186	3.46	HOMO-1→LUMO+3	0.483
				HOMO→LUMO+2	0.483

Supplementary Table S6 λ_{max} values with corresponding oscillator strength (*f*), excitation energy (E) with dominant transition in complexes of undoped/N-doped Cor in THF obtained at B3LYP/6-31++G(d,p) level of theory.

Complexes	λ_{max} in nm	Oscillator strength, f	Excitation energy in eV	Dominant transition	Orbital contribution
Cor···DB	308.9	0.904	4.01	HOMO-1→LUMO	0.484
				HOMO→LUMO+1	0.494
Cor···TB	308.2	0.899	4.02	HOMO-1→LUMO	0.472
				HOMO→LUMO+1	0.473
Cor···PB	308.6	0.034	4.02	HOMO-1→LUMO	0.488
				HOMO→LUMO+1	0.487
$Cor_{(N)}$···DB	389.5	0.034	3.18	(HOMO-1)A→LUMOA	0.498
				(HOMO-1)B→HOMOB	0.715
	583.8	0.030	2.12	HOMOA→(LUMO+4)A	0.968
				(HOMO-2)B →LUMOB	0.124
$Cor_{(N)}$···TB	387.8	0.032	3.20	(HOMO-1)A→LUMOA	0.465
				(HOMO-1)B→HOMOB	0.663
	592.4	0.030	2.09	HOMOA→(LUMO+3)A	0.973
				(HOMO-2)B→LUMOB	0.124
$Cor_{(N)}$···PB	390.0	0.035	3.18	(HOMO-1)A→(LUMO+1)A	0.490
				(HOMO-1)B→LUMOB	0.729
	581.1	0.030	2.13	HOMOA→(LUMO+3)A	0.973
				(HOMO-2)B→LUMOB	0.126
$Cor_{(2N)}$···DB	353.1	0.034	3.51	HOMO-2→LUMO	0.553
				HOMO-1 →LUMO+1	0.394
	548.7	0.124	2.26	HOMO →LUMO+4	0.685
$Cor_{(2N)}$···TB	352.9	0.044	3.51	HOMO-2→LUMO	0.583
				HOMO-1 →LUMO+1	0.364
	555.5	0.112	2.23	HOMO →LUMO+3	0.685
$Cor_{(2N)}$···PB	353.0	0.041	3.51	HOMO-2→LUMO	0.596
				HOMO-1 →LUMO+2	0.319
	544.3	0.114	2.28	HOMO →LUMO+3	0.686
$Cor_{(3N)}$···DB	583.2	0.157	2.13	HOMOA →(LUMO+2)A	0.584
				(HOMO-1)B →(LUMO+3)B	0.761
$Cor_{(3N)}$···TB	589.3	0.148	2.10	HOMOA →(LUMO+2)A	0.582
				(HOMO-1)B →(LUMO+2)B	0.769
$Cor_{(3N)}$···PB	584.5	0.156	2.12	HOMOA →(LUMO+2)A	0.583
				(HOMO-1)B →(LUMO+2)B	0.770

Supplementary Table S7 λ_{max} values with corresponding oscillator strength (*f*), excitation energy (E) with dominant transition in complexes of B-doped Cor in THF obtained at B3LYP/6-31++G(d,p) level of theory

Complexes	λ_{max} in nm	Oscillator strength, f	Excitation energy in eV	Dominant transition	Orbital contribution
$Cor_{(B)}$···DB	342.3	0.087	3.62	(HOMO-2)A→(LUMO+1)A	0.429
				(HOMO-1)B→(LUMO+1)B	0.596
	509.4	0.046	2.43	(HOMO-1)A→LUMOA	0.250
				(HOMO-5)B→HOMOB	0.910
$Cor_{(B)}$···TB	331.5	0.070	3.74	(HOMO-1)A→(LUMO+1) A	0.442
				(HOMO-9)B→HOMOB	0.504
	507.4	0.043	2.44	(HOMO-1)A→LUMOA	0.237
				(HOMO-5)B→HOMOB	0.911
$Cor_{(B)}$···PB	342.4	0.067	3.62	(HOMO-2)A→(LUMO+1)A	0.443
				(HOMO-1)B→(LUMO+1)B	0.600
	507.0	0.043	2.45	(HOMO-1)A→LUMOA	0.243
				(HOMO-5)B→HOMOB	0.909
$Cor_{(2B)}$···DB	301.7	0.515	4.12	HOMO-2→LUMO+2	0.452
				HOMO-1→LUMO+1	0.323
	488.9	0.119	2.54	HOMO-6→LUMO	0.349
				HOMO-4→LUMO	0.583
$Cor_{(2B)}$···TB	303.2	0.332	4.09	HOMO-10→LUMO	0.331
				HOMO-1→LUMO+2	0.277
	488.0	0.112	2.54	HOMO-6→LUMO	0.388
				HOMO-4→LUMO	0.558
$Cor_{(2B)}$···PB	301.9	0.481	4.12	HOMO-2→LUMO+1	0.357
				HOMO-1→LUMO+2	0.406
	489.1	0.111	2.53	HOMO-6→LUMO	0.385
				HOMO-4→LUMO	0.556
$Cor_{(3B)}$···DB	582.8	0.176	2.13	(HOMO-3)A→LUMOA	0.796
				(HOMO-3)B→HOMOB	0.563
$Cor_{(3B)}$···TB	591.2	0.167	2.10	(HOMO-3)A→LUMOA	0.797
				(HOMO-3)B→HOMOB	0.569
$Cor_{(3B)}$···PB	581.2	0.163	2.13	(HOMO-3)A→LUMOA	0.777
				(HOMO-3)B→HOMOB	0.570

Supplementary Table S8 λ_{max} values with corresponding oscillator strength (*f*), excitation energy (E) with dominant transition in complexes of BN-doped Cor in THF obtained at B3LYP/6-31++G(d,p) level of theory.

Complexes	λ_{max} in nm	Oscillator strength, f	Excitation energy in eV	Dominant transition	Orbital contribution
$Cor_{(BN)}$···DB	244.9	0.002	5.06	HOMO→LUMO+7	0.589
				HOMO→LUMO+8	0.305
	328.1	0.542	3.78	HOMO-1→LUMO+1	0.552
				HOMO→LUMO	0.254
$Cor_{(BN)}$···TB	247.9	0.248	5.00	HOMO-2→LUMO+2	0.352
				HOMO→LUMO+7	0.378
	328.9	0.503	3.77	HOMO-1→LUMO+1	0.523
				HOMO→LUMO+2	0.293
$Cor_{(BN)}$···PB	248.5	0.096	4.27	HOMO-2→LUMO+1	0.492
				HOMO→LUMO+3	0.371
	327.1	0.504	3.79	HOMO-1→LUMO+1	0.535
				HOMO→LUMO+2	0.285
$Cor_{(2BN)}$···DB	276.5	0.202	4.48	HOMO-2→LUMO+1	0.138
				HOMO→LUMO+4	0.630
	347.3	0.511	3.57	HOMO-1→LUMO+1	0.554
				HOMO→LUMO+2	0.287
$Cor_{(2BN)}$···TB	280.3	0.208	4.42	HOMO-2→LUMO+1	0.284
				HOMO→LUMO+3	0.575
	346.8	0.511	3.57	HOMO-1→LUMO+1	0.596
				HOMO→LUMO+2	0.233
$Cor_{(2BN)}$···PB	276.2	0.186	4.49	HOMO-2→LUMO+1	0.182
				HOMO→LUMO+3	0.613
	346.8	0.492	3.58	HOMO-1→LUMO+1	0.579
				HOMO→LUMO+2	0.270
$Cor_{(3BN)}$···DB	274.3	0.059	4.52	HOMO-1→LUMO+3	0.243
				HOMO→LUMO+4	0.612
	358.4	1.084	3.46	HOMO-1→LUMO	0.490
				HOMO→LUMO+1	0.488
$Cor_{(3BN)}$···TB	274.7	0.061	4.51	HOMO-1→LUMO+4	0.532
				HOMO→LUMO+2	0.309
	359.0	1.063	3.45	HOMO-1→LUMO	0.379
				HOMO→LUMO+1	0.377
$Cor_{(3BN)}$···PB	274.9	0.084	4.51	HOMO-1→LUMO+4	0.543
				HOMO→LUMO+2	0.339
	358.6	1.076	3.46	HOMO-1→LUMO+1	0.506
				HOMO→LUMO	0.489