Supplementary Material

Designing hybrid materials with advanced optical properties using superalkali M_3O (M = Li, Na, and K) and isoelectronic species of cyclo[18]carbon ($B_6C_6N_6$ and B_9N_9)

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Contents:

Table S1. Cartesian coordinates (in Å) of optimized structures of $B_6C_6N_6$, B_9N_9, $M_3O@B_6C_6N_6$, and $M_3O@B_9N_9$ (M = Li, Na, and K) at the ωB97XD/6-311+G(2d) level……S3

Table S2. Natural population analysis (NPA) charges on the superalkalis ($q(M_3O)$, in e), vertical ionization potentials (E_{VIP}, in eV), vertical electron affinities (E_{VEA}, in eV), dipole moments (μ_0, in D), chemical hardness (η, in eV), and electrophilicity indices (ω, in eV) of $M_3O@B_6C_6N_6$ and $M_3O@B_9N_9$ (M = Li, Na, and K)……S10

Table S3. Interaction energies (ΔE_{int}, in kcal·mol^{-1}) and their components (ΔE_{els}, ΔE_{xrep}, ΔE_{orb}, and ΔE_{disp}, in kcal·mol^{-1}) between M_3O (M = Li, Na, and K) and $B_6C_6N_6$ or B_9N_9 calculated by the sobEDAw method……..……S11

Table S4. Static isotropic polarizabilities (α_{iso}, in a.u.) and their components (α_{xx}, α_{yy}, and α_{zz}, in a.u.) of $M_3O@B_6C_6N_6$ and $M_3O@B_9N_9$ (M = Li, Na, and K) calculated by coupled-perturbed Kohn-Sham (CPKS) method……S12

Table S5. Static first hyperpolarizabilities (β_{tot}, in a.u.) and their Cartesian components (β_x, β_y, and β_z, in a.u.) of $M_3O@B_6C_6N_6$ and $M_3O@B_9N_9$ (M = Li, Na, and K) calculated by coupled-perturbed Kohn-Sham (CPKS) method……S13

Table S6. Dynamic first hyperpolarizabilities ($\beta_{tot}(-\omega;\omega,0)$ and $\beta_{tot}(-2\omega;\omega,\omega)$, in a.u.) of $M_3O@B_6C_6N_6$ and $M_3O@B_9N_9$ (M = Li, Na, and K) calculated by coupled-perturbed Kohn-Sham (CPKS) method……S14

Table S7. Tensorial components of the static first hyperpolarizabilities (in a.u.) of $M_3O@B_6C_6N_6$ and $M_3O@B_9N_9$ (M = Li, Na, and K) calculated by coupled-perturbed Kohn-Sham (CPKS) method……S16

Table S8. Contributions of K_3O unit and $B_6C_6N_6$ or B_9N_9 moiety to the components of the polarizabilities (α_{xx}, in a.u.) and first hyperpolarizabilities (β_{xxx} or β_{zzz}, in a.u.) of $K_3O@B_6C_6N_6$ and $K_3O@B_9N_9$ calculated by finite field (FF) method……S17

Table S1. Cartesian coordinates (in Å) of optimized structures of $B_6C_6N_6$, B_9N_9, $M_3O@B_6C_6N_6$, and $M_3O@B_9N_9$ (M = Li, Na, and K) at the ωB97XD/6-311+G(2d) level

$B_6C_6N_6$ (Charge = 0, Spin multiplicity = 1)			
Atom	*x*	*y*	*z*
B	-2.42323008	2.88398233	0.00000000
C	-1.21503541	3.56761408	0.00000000
N	0.00000000	3.76156079	0.00000000
B	1.28592575	3.54049900	0.00000000
C	2.48216744	2.83601838	0.00000000
N	3.25762875	1.88081638	0.00000000
B	3.70921700	0.65658765	0.00000000
C	3.69716213	-0.73155551	0.00000000
N	3.25760720	-1.88078039	0.00000000
B	2.42319920	-2.88389387	0.00000000
C	1.21498025	-3.56762924	0.00000000
N	0.00002039	-3.76159744	0.00000000
B	-1.28598692	-3.54056998	0.00000000
C	-2.48212672	-2.83605857	0.00000000
N	-3.25760720	-1.88078039	0.00000000
B	-3.70912495	-0.65660513	0.00000000
C	-3.69714768	0.73161087	0.00000000
N	-3.25764914	1.88078107	0.00000000

$Li_3O@B_6C_6N_6$ (Charge = 0, Spin multiplicity = 2)			
Atom	*x*	*y*	*z*
B	-1.14780600	3.64645500	-0.17384300
C	0.27435700	3.73701600	-0.15320200
N	1.43653300	3.46489900	-0.15126200

B	2.59866900	2.77322200	-0.14646100
C	3.33870000	1.64310400	-0.13153200
N	3.75780700	0.44478800	-0.13164300
B	3.67864600	-0.84461500	-0.14046000
C	3.22673200	-2.18205700	-0.16039500
N	2.29938700	-2.98920000	-0.13048100
B	1.13367000	-3.58476100	-0.12769200
C	-0.24396400	-3.73043800	-0.12312600
N	-1.44283800	-3.42427600	-0.11225100
B	-2.59462800	-2.78898600	-0.14530300
C	-3.34862300	-1.62447900	-0.12913100
N	-3.91166800	-0.53110900	-0.19229900
B	-3.61494300	0.78273100	-0.12706800
C	-3.12475600	2.05570000	-0.13906400
N	-2.21484600	2.94023100	-0.12527700
O	-0.01221700	0.06933400	0.98601200
Li	1.58647000	0.57742700	0.80408100
Li	-0.47182900	-1.53625500	0.76368200
Li	-1.23984700	1.22372400	0.87798200

$Na_3O@B_6C_6N_6$ (Charge = 0, Spin multiplicity = 2)			
Atom	*x*	*y*	*z*
B	-3.54744800	-1.47749800	-0.53470800
C	-3.75068700	-0.10585700	-0.53951600
N	-3.80624300	1.12253400	-0.63961000
B	-2.96093400	2.17547400	-0.60597400
C	-1.98144600	3.12378000	-0.65084500
N	-0.76983900	3.50184100	-0.64188600
B	0.49668100	3.66081500	-0.70387900

C	1.83465500	3.16663800	-0.68193300
N	2.78696800	2.44635800	-0.68734300
B	3.61324300	1.37718000	-0.69012900
C	3.73368300	0.02827900	-0.61264300
N	3.59491400	-1.22517600	-0.55857000
B	2.93012500	-2.33557700	-0.51890500
C	1.94382000	-3.33878700	-0.49674100
N	0.77142300	-3.71349600	-0.47409600
B	-0.53508500	-3.79662600	-0.49822000
C	-1.84312100	-3.34175000	-0.49855000
N	-2.79524500	-2.55460300	-0.48961500
O	0.05962100	0.17793100	1.85127400
Na	2.07180400	0.07422100	1.47497800
Na	-1.04560900	-1.47092100	1.33682300
Na	-0.89484400	1.97139900	1.57620600

$K_3O@B_6C_6N_6$ (Charge = 0, Spin multiplicity = 2)			
Atom	*x*	*y*	*z*
B	3.49521000	-2.14093400	-0.49274300
C	2.23531500	-2.69596100	-0.28906600
N	1.08048300	-3.10089500	-0.13013700
B	-0.06393100	-2.27616800	0.16150700
C	-1.51865600	-2.78516900	-0.24827200
N	-2.54421300	-2.28961500	-0.56059700
B	-3.62976000	-1.47311700	-0.80002100
C	-3.93869100	-0.16157500	-0.66535400
N	-4.17337200	1.08906600	-0.50748000
B	-3.17298200	1.97274500	-0.23159900
C	-1.94861900	2.52600500	0.01421500

N	-0.73741000	2.88963300	0.09308800
B	0.55586200	3.01295800	0.06994100
C	1.94096500	2.91373800	-0.07917400
N	3.05905600	2.39527000	-0.27246500
B	4.01558600	1.52901600	-0.48491100
C	4.44138100	0.20454100	-0.57646600
N	4.15057500	-0.99529100	-0.55652900
O	-0.07186700	-1.03787200	0.63894100
K	-2.31896600	-0.18871400	1.74783200
K	2.14621800	0.08046200	1.32968400
K	-0.80309300	0.38476900	-1.58377200

B_9N_9 (Charge = 0, Spin multiplicity = 1)

Atom	*x*	*y*	*z*
B	0.00000000	3.60953800	0.00000000
N	1.31229800	3.60551000	0.00000000
B	2.32016600	2.76506700	0.00000000
N	3.32285600	1.91845200	0.00000000
B	3.55470100	0.62679000	0.00000000
N	3.77861200	-0.66627100	0.00000000
B	3.12595200	-1.80476900	0.00000000
N	2.46631400	-2.93923800	0.00000000
B	1.23453500	-3.39185600	0.00000000
N	0.00000000	-3.83690300	0.00000000
B	-1.23453500	-3.39185600	0.00000000
N	-2.46631400	-2.93923800	0.00000000
B	-3.12595200	-1.80476900	0.00000000
N	-3.77861200	-0.66627100	0.00000000
B	-3.55470100	0.62679000	0.00000000

N	-3.32285600	1.91845200	0.00000000
B	-2.32016600	2.76506700	0.00000000
N	-1.31229800	3.60551000	0.00000000

$Li_3O@B_9N_9$ (Charge = 0, Spin multiplicity = 2)			
Atom	*x*	*y*	*z*
B	-2.00471300	-3.03602300	-0.05798300
N	-3.20538900	-2.51999500	-0.09046800
B	-3.78597700	-1.33660800	-0.10839200
N	-4.34783100	-0.15493700	-0.12253800
B	-3.93935900	1.10036100	-0.09631400
N	-3.51537600	2.33724400	-0.06600500
B	-2.33588300	2.93535600	-0.01355800
N	-1.16604000	3.50690100	0.05193800
B	0.12315600	3.17930900	0.01766300
N	1.34783800	2.74408300	0.06062500
B	2.53633200	2.57557100	-0.67458700
N	3.36970800	1.43668200	-0.64516400
B	3.27196700	0.20794300	-1.04662800
N	3.18354400	-1.09964500	-1.35252400
B	2.46055500	-1.95066600	-0.67898100
N	1.73881100	-2.84839900	0.00856500
B	0.46792300	-3.20655300	-0.04913100
N	-0.79267100	-3.55152100	-0.01758100
O	2.33200100	-0.16141800	1.87980000
Li	1.28940100	1.04986500	1.24349900
Li	3.68116100	0.76287400	1.36514500
Li	2.05805000	-1.81440400	1.96242900

$Na_3O@B_9N_9$ (Charge = 0, Spin multiplicity = 2)			
Atom	*x*	*y*	*z*
O	0.16038100	-0.00032900	1.81616300
Na	2.11061500	0.00203200	1.02018200
Na	-0.57478300	-1.90337300	2.02665300
Na	-0.57951600	1.90092100	2.02632000
B	-3.50713700	-1.22456500	-0.86598800
N	-3.97350900	-0.00351500	-0.99178800
B	-3.50961100	1.21844400	-0.86575200
N	-3.05860800	2.44519500	-0.72712400
B	-1.90469100	3.02690000	-0.48406700
N	-0.77135800	3.57923800	-0.12139000
B	0.52644300	3.45727200	-0.42474800
N	1.79529900	3.32126900	-0.62740000
B	2.65088800	2.28338100	-0.75370000
N	3.40463900	1.24803600	-0.78530400
B	3.79362500	0.00377500	-1.28640500
N	3.40689400	-1.24123000	-0.78538400
B	2.65504700	-2.27796200	-0.75382600
N	1.80155600	-3.31762000	-0.62776700
B	0.53291200	-3.45598200	-0.42525500
N	-0.76465800	-3.58061500	-0.12200600
B	-1.89892900	-3.03013300	-0.48463400
N	-3.05386300	-2.45052800	-0.72785600

$K_3O@B_9N_9$ (Charge = 0, Spin multiplicity = 2)			
Atom	*x*	*y*	*z*
B	-0.05023400	-3.62987000	-0.80405800
N	-1.33931400	-3.55550100	-0.53412000

B	-2.36309200	-2.76555100	-0.79568000
N	-3.39410700	-1.98419500	-0.97798100
B	-3.63770900	-0.70529900	-1.21674700
N	-3.89062400	0.55450000	-1.43684600
B	-3.20037700	1.69109700	-1.45552000
N	-2.52771600	2.79981900	-1.41952800
B	-1.25224000	3.20112900	-1.25889000
N	-0.05437600	3.53045100	-0.93849500
B	1.16797900	3.14117900	-0.43213900
N	2.34064000	2.63644300	-0.95395600
B	3.02555200	1.60216000	-1.28108700
N	3.72335400	0.46224300	-1.44730200
B	3.50306900	-0.81579200	-1.48186800
N	3.27899200	-2.12657000	-1.46109400
B	2.26181600	-2.91041500	-1.23599000
N	1.23979300	-3.71526300	-0.99211800
O	0.04671900	0.07462900	1.96569700
K	-0.74262100	-2.05769700	2.28904800
K	2.27487600	0.78493700	1.61384400
K	-1.17878400	2.06993300	1.63470800

Table S2. Natural population analysis (NPA) charges on the superalkalis ($q(M_3O)$, in e), vertical ionization potentials (E_{VIP}, in eV), vertical electron affinities (E_{VEA}, in eV), dipole moments (μ_0, in D), chemical hardness (η, in eV), and electrophilicity indices (ω, in eV) of $M_3O@B_6C_6N_6$ and $M_3O@B_9N_9$ (M = Li, Na, and K)

	$q(M_3O)$	E_{VIP}	E_{VEA}	μ_0	η	ω
$Li_3O@B_6C_6N_6$	0.98	7.17	2.36	1.30	4.82	2.36
$Na_3O@B_6C_6N_6$	0.99	6.64	2.22	3.80	4.42	2.22
$K_3O@B_6C_6N_6$	1.76	5.60	1.77	5.89	3.83	1.77
$Li_3O@B_9N_9$	0.99	8.09	0.16	5.74	7.93	1.07
$Na_3O@B_9N_9$	0.98	6.64	0.32	9.06	6.33	0.96
$K_3O@B_9N_9$	0.95	5.86	0.22	9.43	5.64	0.82

Table S3. Interaction energies (ΔE_{int}, in kcal·mol^{-1}) and their components (ΔE_{els}, ΔE_{xrep}, ΔE_{orb}, and ΔE_{disp}, in kcal·mol^{-1}) between M_3O (M = Li, Na, and K) and $B_6C_6N_6$ or B_9N_9 calculated by the sobEDAw method

	ΔE_{int}	ΔE_{els}	ΔE_{xrep}	ΔE_{orb}	ΔE_{disp}
$Li_3O@B_6C_6N_6$	-117.5	-89.6	23.7	-33.7	-17.3
$Na_3O@B_6C_6N_6$	-99.8	-84.1	20.4	-17.4	-18.1
$K_3O@B_6C_6N_6$	-262.3	-375.6	613.2	-446.8	-50.6
$Li_3O@B_9N_9$	-128.3	-127.9	47.5	-30.9	-16.2
$Na_3O@B_9N_9$	-102.6	-96.3	26.6	-15.7	-16.5
$K_3O@B_9N_9$	-85.9	-82.7	24.6	-11.2	-16.1

Table S4. Static isotropic polarizabilities (α_{iso}, in a.u.) and their components (α_{xx}, α_{yy}, and α_{zz}, in a.u.) of $M_3O@B_6C_6N_6$ and $M_3O@B_9N_9$ (M = Li, Na, and K) calculated by coupled-perturbed Kohn-Sham (CPKS) method

	α_{iso}	α_{xx}	α_{yy}	α_{zz}
$Li_3O@B_6C_6N_6$	387	524	503	134
$Na_3O@B_6C_6N_6$	413	546	529	165
$K_3O@B_6C_6N_6$	407	626	431	164
$Li_3O@B_9N_9$	221	271	244	148
$Na_3O@B_9N_9$	244	292	269	171
$K_3O@B_9N_9$	267	301	298	204

Table S5. Static first hyperpolarizabilities (β_{tot}, in a.u.) and their Cartesian components (β_x, β_y, and β_z, in a.u.) of $M_3O@B_6C_6N_6$ and $M_3O@B_9N_9$ (M = Li, Na, and K) calculated by coupled-perturbed Kohn-Sham (CPKS) method

	β_{tot}	β_x	β_y	β_z
$Li_3O@B_6C_6N_6$	1054	-402	-932	-283
$Na_3O@B_6C_6N_6$	1125	-747	-178	-822
$K_3O@B_6C_6N_6$	3040	-3039	-42	-62
$Li_3O@B_9N_9$	846	-536	-627	-186
$Na_3O@B_9N_9$	835	-22	6	-835
$K_3O@B_9N_9$	3479	-69	-376	-3458

Table S6. Dynamic first hyperpolarizabilities ($\beta_{tot}(-\omega;\omega,0)$ and $\beta_{tot}(-2\omega;\omega,\omega)$, in a.u.) of $M_3O@B_6C_6N_6$ and $M_3O@B_9N_9$ (M = Li, Na, and K) calculated by coupled-perturbed Kohn-Sham (CPKS) method

	ω	$\beta_{tot}(-\omega;\omega,0)$	$\beta_{tot}(-2\omega;\omega,\omega)$
$Li_3O@B_6C_6N_6$	0.01	1121	1394
	0.02	682	593
	0.03	16919	55181
	0.04	1188	70109
	0.05	1216	7676
	0.06	28554	243522
	0.07	194807	465172
	0.08	1976539	87706370
	0.09	13344	77472
	0.10	10940	97160
	0.11	241362	700686
	0.12	26178	47421
$Na_3O@B_6C_6N_6$	0.01	2290	2408
	0.02	1112	851
	0.03	111323	1846893
	0.04	1211	7391
	0.05	1546	3488
	0.06	18166	53194
	0.07	1485713	58463
	0.08	718819	261516
	0.09	15528	18161
	0.10	136631	372138
	0.11	109796	866888
	0.12	23638	45072
$K_3O@B_6C_6N_6$	0.01	3169	4283
	0.02	5626	17146
	0.03	8919	53948
	0.04	6642	48558
	0.05	25341	363152
	0.06	74792	12736
	0.07	83958	128638
	0.08	100756	218251
	0.09	130512	195790
	0.10	601785	2057776
	0.11	606638	291482
	0.12	27669	141706
$Li_3O@B_9N_9$	0.01	852	865
	0.02	872	929

	0.03	906	1060
	0.04	960	1377
	0.05	1038	1757
	0.06	1150	2423
	0.07	1298	2092
	0.08	1216	9968
	0.09	10022	8634
	0.10	1192	20528
	0.11	4479	5038
	0.12	6522	9920
$Na_3O@B_9N_9$	0.01	849	876
	0.02	891	1022
	0.03	969	1382
	0.04	1100	2742
	0.05	1318	10618
	0.06	1706	8362
	0.07	2550	23255
	0.08	9884	11809
	0.09	11055	85526
	0.10	54575	33876
	0.11	144588	37489
	0.12	967991	306295
$K_3O@B_9N_9$	0.01	3538	3662
	0.02	3726	4321
	0.03	4079	6022
	0.04	4679	12271
	0.05	5704	36977
	0.06	7581	79027
	0.07	11589	69167
	0.08	23446	34177
	0.09	64659	18673
	0.10	2894111	737087
	0.11	71701	24360
	0.12	456687	4587363

Table S7. Tensorial components of the static first hyperpolarizabilities (in a.u.) of $M_3O@B_6C_6N_6$ and $M_3O@B_9N_9$ (M = Li, Na, and K) calculated by coupled-perturbed Kohn-Sham (CPKS) method

	β_{xxx}	β_{xyy}	β_{xzz}	β_{xxy}	β_{yyy}	β_{yzz}	β_{xxz}	β_{yyz}	β_{zzz}
$K_3O@B_6C_6N_6$	-2128	-1046	135	115	-173	16	70	-168	35
$K_3O@B_9N_9$	440	-369	-140	233	-130	-479	-250	-748	-2461

Table S8. Contributions of K_3O unit and $B_6C_6N_6$ or B_9N_9 moiety to the components of the polarizabilities (α_{xx}, in a.u.) and first hyperpolarizabilities (β_{xxx} or β_{zzz}, in a.u.) of $K_3O@B_6C_6N_6$ and $K_3O@B_9N_9$ calculated by finite field (FF) method

	α_{xx}	β_{xxx}		α_{xx}	β_{zzz}
$K_3O@B_6C_6N_6$	625	-2201	$K_3O@B_9N_9$	300	-1968
K_3O	34	151	K_3O	58	-1917
$B_6C_6N_6$	591	-2352	B_9N_9	242	-51