Supporting Information

for

Crystal engineering of cation-radical salts with weakly-coordinating carbadodecaborate anions

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Details of X-ray structures' analysis

The length of C-H and B-H carborane bonds were refined. B-H bond distances within each structure were restrained to be similar to each other. Other H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms, with C-H bond distances of 0.95 Å for aromatic moieties and 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH_2 and CH_3 moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. $U_{iso}(H)$ values were set to a multiple of $U_{eq}(C/B)$ with 1.5 for CH_3, and 1.2 for all others.

The crystal under investigation for (2) was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now, with the two components being related by a 180° rotation around the reciprocal a-axis. The two components were integrated using Saint and corrected for absorption using twinabs, resulting in the following statistics:

9717 data (2176 unique) involve domain 1 only, mean I/sigma 28.8
9762 data (2185 unique) involve domain 2 only, mean I/sigma 28.6
3893 data (1070 unique) involve 2 domains, mean I/sigma 47.0
The exact twin matrix identified by the integration program was found to be:
 0.99992 -0.00015 0.32678
-0.00051 -1.00000 0.00026
 0.00050 -0.00013 -0.99992

The structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones), resulting in a BASF value of 0.493(2). The R_{int} value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Sheldrick, 2012)).

The carbon atom of the carborane anion was refined as 1:1 disordered over two symmetry equivalent positions with a boron atom. The positions and the ADPs of the boron and carbon atom were constrained to be each identical. Partial other locations of the C atom (disordered with other boron atoms) cannot be positively excluded. The H atoms of one methyl group was refined as disordered (AFIX 127). The occupancy ratio refined to 0.63(3) to 0.37(3).

In the structure of (4), both anion and cation are disordered around crystallographic inversion centers. For the cation, pairs of carbon atoms related by approximate inversion symmetry were constrained to have identical ADPs C2 C9, C3 C10, C4 C11, C5 C12). For the anion, inversion disorder was modelled for the entire anion (not just the pair of C and B atoms necessarily breaking exact inversion symmetry). Once disorder was modelled need for inclusion of a second pair of inversion related moieties was apparent (i.e. four fold disorder). To model disorder, all B-B and B-C(cage) bond lengths were restrained to be similar in length. The two not equivalent disordered moieties were also restrained to have similar geometries. U_{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. For the minor moiety, U_{ij} components of ADPs of methyl C atoms related by crystallographic

symmetry were also restrained to be similar. Subject to these conditions the occupancy ratio refined to two times 0.340(4) to two times 0.160(4). Additional apparent disorder for both anion and cation was not sufficiently resolved and was not modelled.

In (5), an acetonitrile molecule is disordered around a mirror plane. U_{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar.
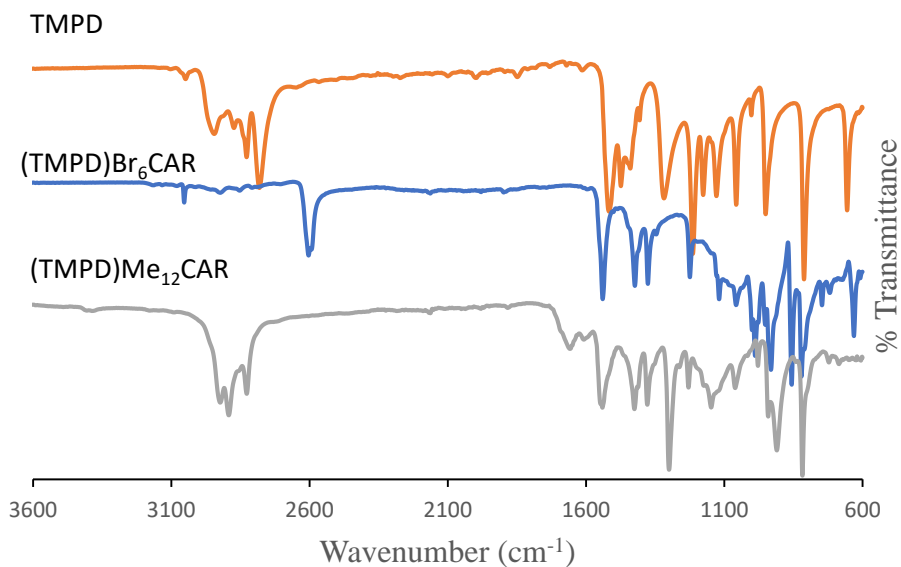
Figure S1. FT-IR spectra of TMPD, $(TMPD)Br_6CAR$, and $(TMPD)Me_{12}CAR$.
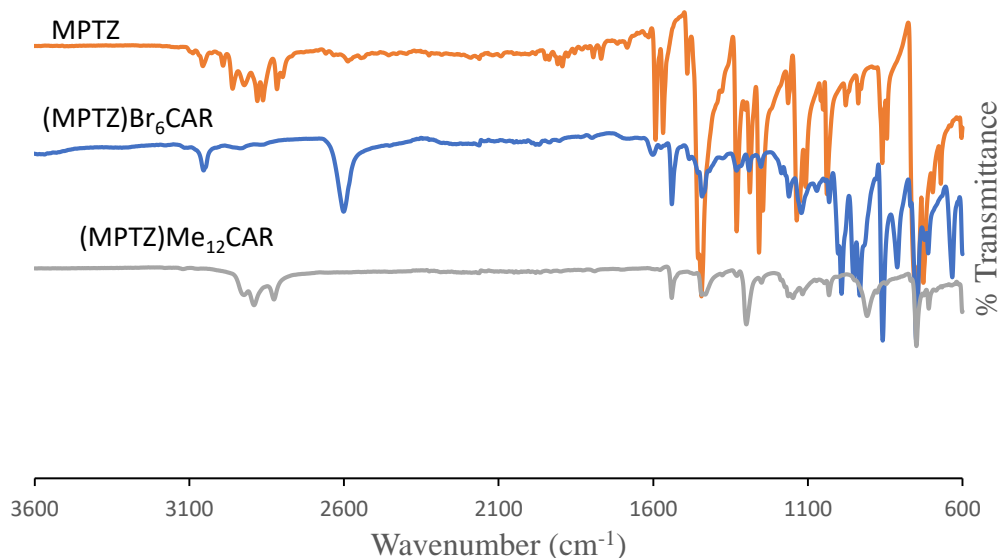
Figure S2. FT-IR spectra of MPTZ, $(MPTZ)Br_6CAR$, and $(MPTZ)Me_{12}CAR$.
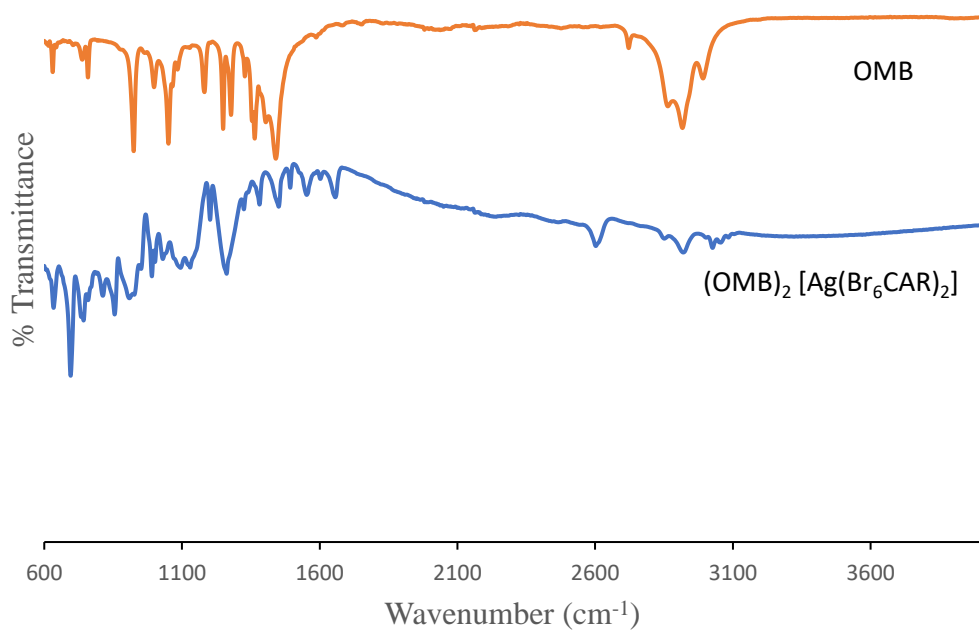
Figure S3. FT-IR spectra of OMB and (OMB)[Ag(Br$_6$CAR)$_2$].
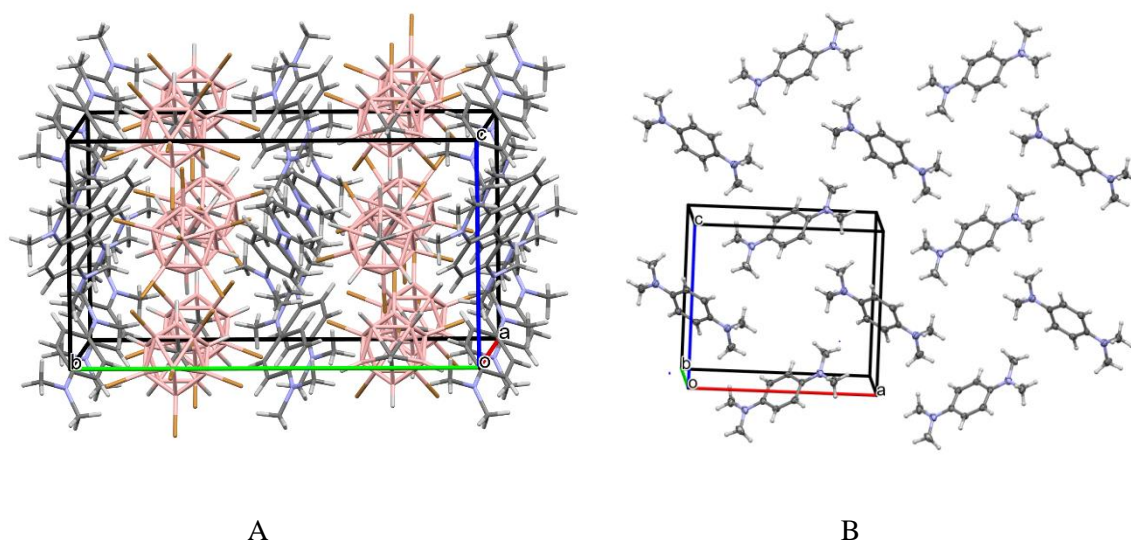

A   B

Figure S4. The crystal lattice of (TMPD)Br$_6$CAR (**A**) comprising layers of essentially isolated TMPD$^{+\bullet}$ cation radicals (showing no contacts shorter than van der Waals separations).

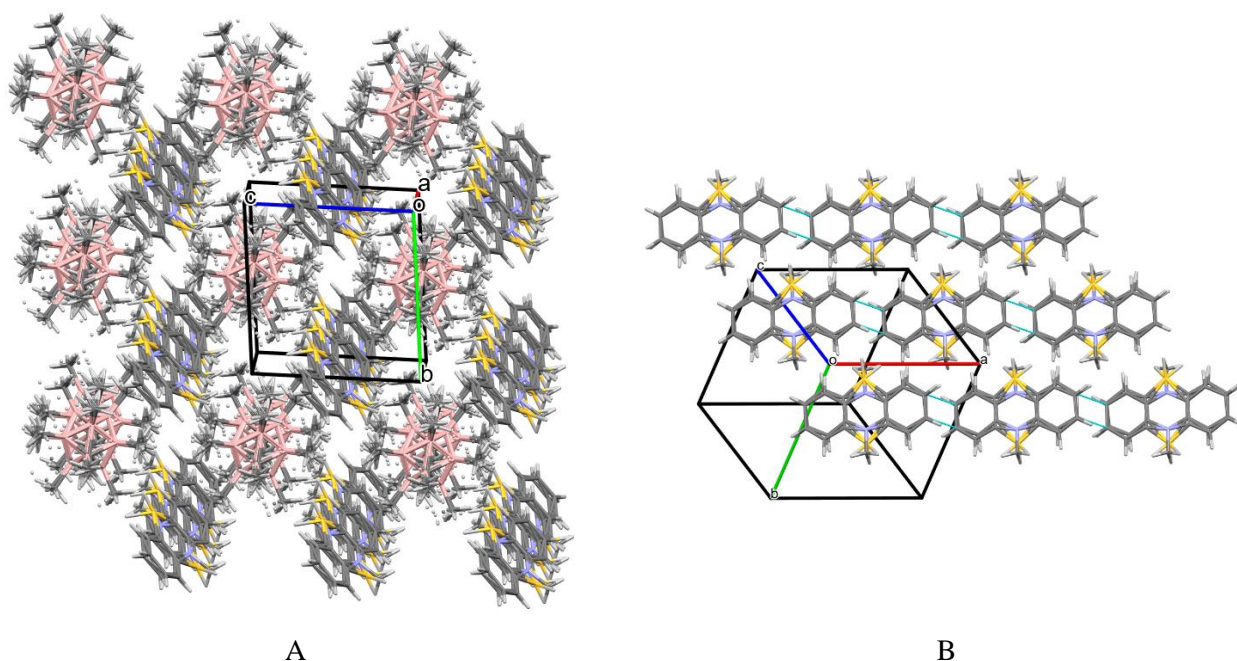<center>A   B</center>

Figure S5. The crystal lattice of (MPTZ)Me$_{12}$CAR (**A**) comprising essentially isolated MPTZ$^{+\bullet}$ cation radicals (**B**). Light blue lines indicate contacts shorter than the van der Waals separations.

Table S1. Energies (in Hartree) of the D$^{+\bullet}$ monomers and D$_2^{2+}$ dimers resulting from the UM06L/def2TZVPP computations in acetonitrile (unless noted otherwise) .

	TMPD	MPTZ	OMB
D$^{+\bullet}$	-500.1422190	-954.9124800	-776.5672000
D$_2^{2+}$ (singlet)	-1000.293959	-1909.838787	-1553.166240
D$_2^{2+}$ (triplet)[a]	-1000.281002	-1909.824602	-1553.138863

    a) Energy of triplet in the geometry of the optimized singlet; b)

Table S2. Energies (in Hartree) for calculation of dispersion in the dimers[a]

		B98	B97D
TMPD	Monomers	-500.009	-499.8599328
	Dimers	-1000	-999.740593
MPTZ	Monomers	-954.724	-954.5856412
	Dimers	-1909.43	-1909.193121
OMB	Monomers	-776.334	-776.0895865
	Dimers	-1552.65	-1552.225872

    a) Energies obtained from single-point calculations using indicated method and def2tzvpp basis set using coordinates of the monomers and dimers optimized via UM06L/def2tzvpp calculations in CH$_3$CN.

Table S3. Atomic coordinates (in Å) and ESP charges (in a.u.) which were used in calculations of electrostatic interaction between monomers in π-dimers.

(TMPD)$_2^{2+}$

Atom	Charge	Coordinates		
C	-0.15202	0.681072	-1.09403	-1.35947
H	0.127364	1.190956	-0.7419	-2.24123
C	-0.1518	-0.68128	-1.0939	-1.35944
H	0.127324	-1.19112	-0.74165	-2.24118
C	0.259829	-1.42423	-1.57586	-0.25001
N	-0.06506	-2.77325	-1.58234	-0.25234
C	-0.05024	-3.53042	-1.26879	-1.45311
H	0.088261	-3.52683	-2.10828	-2.14949
H	0.038185	-3.12434	-0.40107	-1.96127
H	0.095456	-4.55548	-1.05139	-1.17526
C	-0.13651	-3.51706	-2.19411	0.836605
H	0.102932	-3.42757	-3.28047	0.816674
H	0.108348	-4.56303	-1.93072	0.737601
H	0.097	-3.16513	-1.83867	1.801506
C	-0.14163	-0.68012	-2.08468	0.853214
H	0.128079	-1.19498	-2.49715	1.70571
C	-0.14232	0.67979	-2.08481	0.85319
H	0.128456	1.194612	-2.49735	1.705672
C	0.260279	1.423958	-1.57613	-0.25007
N	-0.06531	2.772972	-1.58286	-0.25242
C	-0.13618	3.516643	-2.19475	0.836562
H	0.096809	3.165518	-1.8383	1.801403
H	0.102795	3.425971	-3.28101	0.817401
H	0.108349	4.562845	-1.93253	0.736917
C	-0.0501	3.530163	-1.26906	-1.4531
H	0.038123	3.123915	-0.40137	-1.96118
H	0.095401	4.555162	-1.05143	-1.17516
H	0.088254	3.526796	-2.10849	-2.14956
C	-0.14231	0.680111	2.084987	-0.85323
H	0.128427	1.194943	2.49762	-1.70565
C	-0.14241	-0.67979	2.085029	-0.85322
H	0.128434	-1.19461	2.497684	-1.70564
C	0.261151	-1.42395	1.576157	0.249971
N	-0.06621	-2.77296	1.582617	0.25237
C	-0.13602	-3.51698	2.194248	-0.83651
H	0.096805	-3.16489	1.839093	-1.80145
H	0.102831	-3.42798	3.280644	-0.8164
H	0.108304	-4.56284	1.930362	-0.73759
C	-0.04942	-3.52993	1.268767	1.453171
H	0.037842	-3.12372	0.400909	1.961004

H	0.095306	-4.55505	1.05143	1.17545
H	0.088126	-3.52622	2.108063	2.149792
C	-0.15229	-0.68103	1.094109	1.359379
H	0.127485	-1.1909	0.74192	2.241123
C	-0.15223	0.681316	1.094061	1.359369
H	0.127437	1.191176	0.741827	2.2411
C	0.260997	1.424247	1.576086	0.249959
N	-0.06612	2.773261	1.582556	0.252356
C	-0.0495	3.530274	1.268755	1.453146
H	0.088155	3.526656	2.108103	2.149697
H	0.037923	3.124058	0.400944	1.961055
H	0.095288	4.555347	1.051276	1.175373
C	-0.13601	3.517222	2.194247	-0.83653
H	0.10281	3.427895	3.280618	-0.8166
H	0.108328	4.563151	1.930706	-0.73745
H	0.09679	3.165339	1.838839	-1.80146

(MPTZ)$_2^{2+}$

Atom	Charge		Coordinates	
S	0.029845	-1.34536	-0.68067	-1.72731
N	-0.35179	0.98548	1.332436	-1.25181
C	0.388299	-0.30283	1.839218	-1.25553
C	-0.26534	-0.54055	3.21377	-1.0752
H	0.166445	0.284016	3.899446	-0.98854
C	0.033792	-1.81828	3.720599	-1.06026
H	0.108187	-1.9549	4.784467	-0.936
C	-0.09512	-2.9275	2.887331	-1.21226
H	0.125854	-3.92687	3.294176	-1.19236
C	-0.0717	-2.73451	1.542353	-1.40129
H	0.136883	-3.57479	0.876348	-1.5394
C	0.03771	-1.43983	1.006948	-1.44066
C	0.307249	1.31712	0.059961	-1.70152
C	-0.18284	2.658383	-0.28495	-1.9364
H	0.141113	3.436632	0.448059	-1.81432
C	0.007694	3.003451	-1.54654	-2.36337
H	0.109983	4.044448	-1.77042	-2.54329
C	-0.07602	2.03111	-2.5252	-2.57699
H	0.117713	2.309757	-3.51285	-2.91157
C	-0.04867	0.709809	-2.21368	-2.37111
H	0.133144	-0.06435	-2.94894	-2.54123
C	0.000819	0.340607	-0.93477	-1.9409
C	0.103839	2.088284	2.22527	-0.88892
H	0.091965	2.520524	2.695179	-1.77021
H	0.015379	2.852427	1.660526	-0.36786

Atom	Charge		Coordinates	
H	0.03161	1.735594	2.987736	-0.21081
S	0.033196	-1.26033	0.88762	1.732838
N	-0.36916	0.726752	-1.47175	1.265591
C	0.31585	1.252001	-0.26874	1.723732
C	-0.19488	2.627927	-0.14278	1.976377
H	0.144304	3.280922	-0.99035	1.862311
C	0.022284	3.165624	1.047229	2.409985
H	0.105272	4.226675	1.100694	2.603415
C	-0.08267	2.360249	2.168972	2.613185
H	0.118675	2.789424	3.099391	2.952524
C	-0.04775	1.008521	2.072578	2.391545
H	0.133276	0.359934	2.922133	2.554763
C	0.005326	0.444303	0.869163	1.954904
C	0.406986	-0.62576	-1.76172	1.240566
C	-0.25203	-1.08006	-3.07802	1.038842
H	0.160279	-0.37546	-3.8866	0.954635
C	0.020114	-2.42191	-3.37244	0.999318
H	0.11246	-2.72604	-4.39901	0.85909
C	-0.09329	-3.38469	-2.37274	1.147091
H	0.125241	-4.43628	-2.61252	1.109139
C	-0.05804	-2.98023	-1.0789	1.35609
H	0.13439	-3.70484	-0.28869	1.494675
C	0.018414	-1.61696	-0.75883	1.419927
C	0.095795	1.676776	-2.53158	0.918277
H	0.093732	2.004529	-3.07143	1.804431
H	0.037096	1.22269	-3.22154	0.22298
H	0.019068	2.534929	-2.0968	0.42016

(OMB)₂²⁺

Atom	Charge		Coordinates	
C	0.030072	-2.02612	0.178736	1.090229
C	-0.06899	-3.0976	1.051484	1.176401
C	0.0888	-4.33479	0.488403	0.813859
C	0.024493	-4.45462	-0.85291	0.349908
C	0.011114	-3.36391	-1.74678	0.30829
C	0.009422	-2.16021	-1.18269	0.669073
C	0.107965	-0.73187	-1.40411	0.919813
C	-0.1043	0.293423	-2.32334	0.960707
C	0.089512	1.487719	-1.81503	1.513011
C	0.016037	1.620088	-0.4561	1.964899
C	0.068214	0.550872	0.456063	1.943015
C	-0.03519	-0.60491	-0.04033	1.375556
C	0.141086	-2.95737	2.472093	1.62905
C	-0.096	-5.58486	1.315051	0.932284

C	-0.06467	-5.8021	-1.3365	-0.09779
C	-0.06741	-3.53391	-3.1873	-0.06957
C	0.118794	0.12904	-3.74922	0.52028
C	-0.0921	2.65362	-2.72523	1.739964
C	-0.20976	2.933272	-0.04851	2.556238
C	-0.07321	0.687628	1.846884	2.478257
H	0.008746	-3.57318	3.145263	1.035347
H	-0.02686	-1.92607	2.798763	1.541796
H	0.026986	-3.26059	2.580855	2.671896
H	0.048765	-6.4054	0.719678	1.328097
H	0.079868	-5.90275	1.68956	-0.04483
H	0.0433	-5.44131	2.167842	1.587619
H	0.042509	-6.34813	-0.55375	-0.62005
H	0.07922	-6.4062	-1.63464	0.764019
H	0.038534	-5.71907	-2.19422	-0.75801
H	0.053131	-4.39572	-3.61843	0.437737
H	0.03807	-2.66032	-3.76694	0.209987
H	0.074085	-3.69756	-3.30155	-1.14337
H	0.00074	1.017597	-4.12928	0.022735
H	-0.0116	-0.69774	-3.84141	-0.17706
H	0.031554	-0.0718	-4.39636	1.375681
H	0.035556	3.546892	-2.35869	1.230227
H	0.062844	2.462039	-3.74166	1.418334
H	0.077299	2.898037	-2.74544	2.804056
H	0.057521	3.764135	-0.35762	1.920056
H	0.120181	3.080212	-0.53857	3.522224
H	0.083136	3.003083	1.023568	2.707058
H	0.07069	1.035435	1.833475	3.510724
H	0.039367	-0.25866	2.375399	2.45023
H	0.032446	1.418715	2.415786	1.89842
C	0.029991	2.026124	-0.17872	-1.09022
C	-0.06893	3.097609	-1.05145	-1.17642
C	0.088781	4.334793	-0.48837	-0.81386
C	0.024514	4.454612	0.852933	-0.34987
C	0.011056	3.36389	1.746795	-0.30824
C	0.009501	2.160203	1.182709	-0.66905
C	0.107823	0.731867	1.404121	-0.91984
C	-0.10408	-0.29343	2.323348	-0.96078
C	0.089292	-1.48772	1.815002	-1.51307
C	0.016208	-1.62008	0.456052	-1.96489
C	0.068106	-0.55086	-0.45611	-1.94295
C	-0.03507	0.604909	0.040325	-1.37553
C	0.140996	2.957379	-2.47204	-1.62912
C	-0.09597	5.58488	-1.315	-0.93231

C	-0.06467	5.802089	1.336528	0.097835
C	-0.06737	3.533879	3.187312	0.069654
C	0.118647	-0.12906	3.749246	-0.52041
C	-0.09199	-2.65363	2.725182	-1.74005
C	-0.20995	-2.93327	0.048426	-2.55622
C	-0.07314	-0.68758	-1.84696	-2.47813
H	0.008784	3.573171	-3.14524	-1.03543
H	-0.02682	1.926071	-2.7987	-1.54189
H	0.027	3.260607	-2.58077	-2.67197
H	0.048758	6.405411	-0.7196	-1.3281
H	0.079866	5.902764	-1.68953	0.0448
H	0.043286	5.441348	-2.16777	-1.58767
H	0.042508	6.348122	0.553766	0.620076
H	0.079216	6.406187	1.634699	-0.76396
H	0.038533	5.719047	2.194222	0.758088
H	0.053122	4.39567	3.618463	-0.43767
H	0.038048	2.660265	3.766938	-0.20987
H	0.074081	3.697555	3.30154	1.143446
H	0.000754	-1.01763	4.12931	-0.02289
H	-0.01155	0.697715	3.841472	0.176926
H	0.031593	0.071767	4.396356	-1.37584
H	0.03558	-3.5469	2.358658	-1.23029
H	0.062867	-2.46205	3.741633	-1.41845
H	0.077198	-2.89805	2.745355	-2.80414
H	0.057574	-3.76413	0.357569	-1.92005
H	0.120263	-3.0802	0.538447	-3.52223
H	0.083157	-3.00308	-1.02365	-2.70699
H	0.070669	-1.03535	-1.83361	-3.51061
H	0.03934	0.258713	-2.37546	-2.45004
H	0.032449	-1.41869	-2.41584	-1.89829

Table S4. Energies of the $D^{+\bullet}$ monomers and D_2^{2+} dimers resulting from the single-point UM06L/def2TZVPP computations[a]

	Medium	TMPD	MPTZ	OMB
E(D$^{+\bullet}$), Hartree	CH_2Cl_2	-500.136861	-954.906906	-776.561636
E(D$_2^{2+}$), Hartree	CH_2Cl_2	-1000.276056	-1909.821196	-1553.147749
ΔE,[b] kJ/mol	CH_2Cl_2	4.4	-13.8	-53.3
E(D$^{+\bullet}$), Hartree	vacuum	-500.136861	-954.849084	-776.512135
E(D$_2^{2+}$), Hartree	vacuum	-1000.276056	-1909.634876	-1552.982463
ΔE,[b] kJ/mol	vacuum	205.6	171.6	109.7

a) Using coordinates of the species optimized in acetonitrile; b) Including difference of ZPE of monomers and dimers calculated using data in acetonitrile.

Table S5. Electron density, $\rho(\mathbf{r})$, at the BCPs at the bond paths between monomers in the π-bonded dimers.[a]

π-dimer	$\rho(\mathbf{r})$, a.u.			
TMPD$_2{}^{2+}$	0.0090[a]	0.0090[a]	0.0072[b]	0.0072[b]
MPTZ$_2{}^{2+}$	0.0068[c]	0.0067[c]	0.0134[d]	0.0128[d]
OMB$_2{}^{2+}$	0.0124[e]	0.0124[e]	0.0106[e]	0.0106[e]

a) C-C bond path; b) N-N bond path; c) C-N bond path; d) C-S bond path;
e) C-C bond path between OMB core.