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Supporting information for:

Direct probing of ion pair formation using a symmetric triangulenium dye

Fredrik Westerlund,[a,b] Jonas Elm,[a] Jacob Lykkebo,[a] Nils Carlsson,[b] Erling Thyrhaug,[a] Björn Åkerman,[b] Thomas Just Sørensen,[a] Kurt V. Mikkelsen[a] and Bo W. Laursen*[a]

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Absorption spectra in DCM

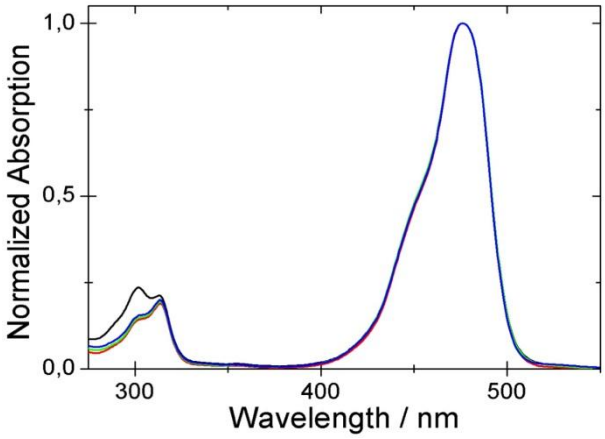

Figure S1. Normalized absorption spectra of $ATOTA^+$ in DCM with four different counterions, Cl^- (black), BF_4^- (red), PF_6^- (green) and TT^- (blue) measured in ca $5 \cdot 10^{-5}$ M^{-1} solutions. The spectra are identical, except for the intrinsic absorption of the TT^- anion at around 300 nm.

Concentration dependence of ion-pair formation

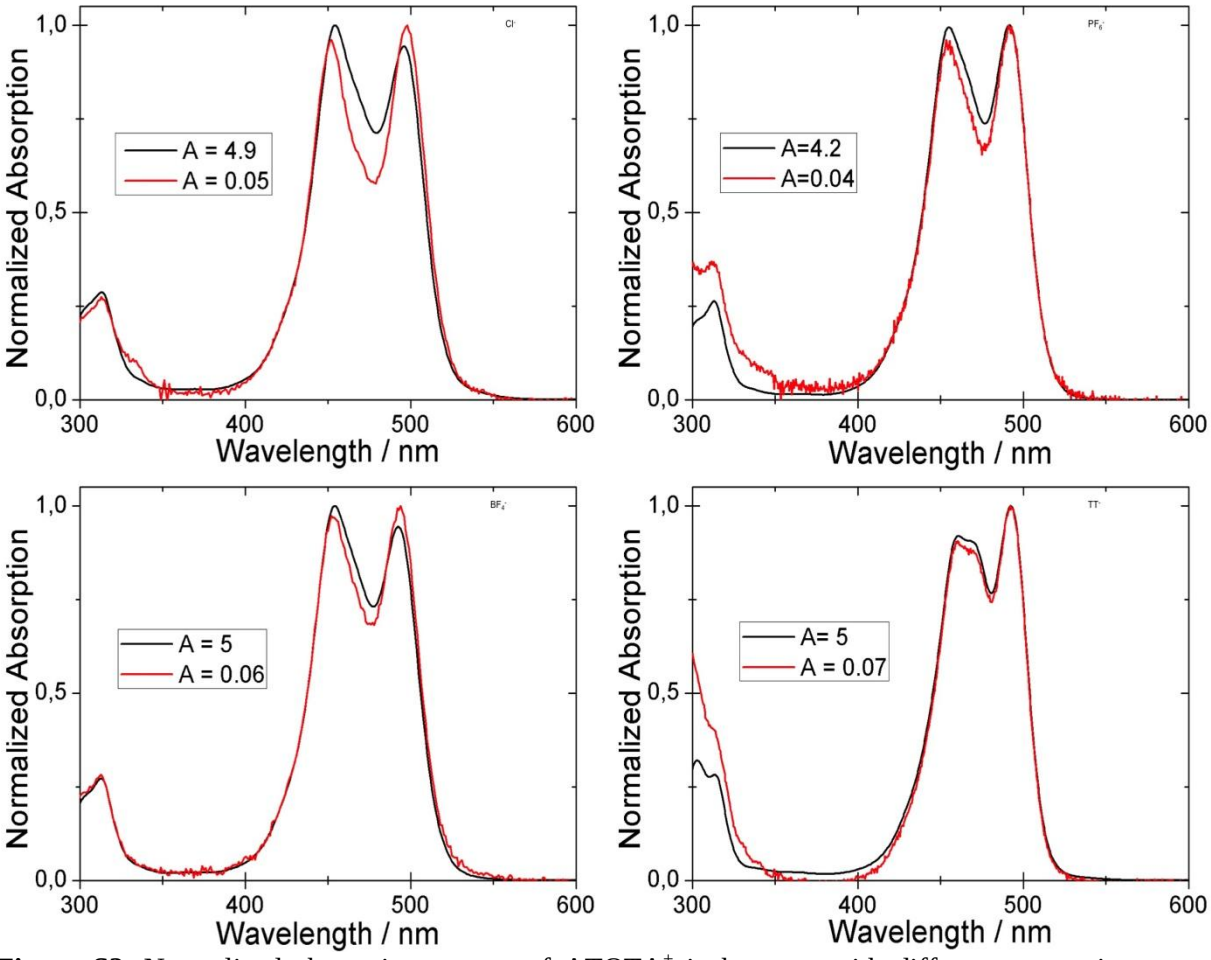

Figure S2. Normalized absorption spectra of ATOTA$^+$ in benzene with different counterions at varying concentrations as indicated in each panel. The spectra are relatively insensitive to the concentration with the largest difference observed with Cl^- as counterion, indicating that it has the largest tendency to for ion pair dimers.

Solvent titration experiments

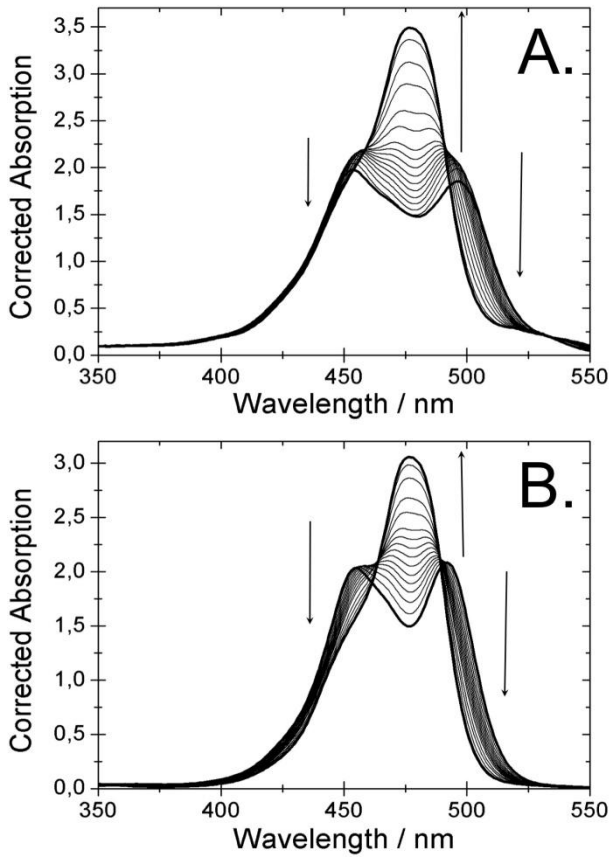

Figure S3. Titration of ATOTA·Cl (A.) and ATOTA·PF_6 (B.) in benzene with increasing amounts of DCM. The titration starts in pure benzene and ends in approximately 60 volume percent DCM. The two extreme spectra are shown in bold. The arrows point out the change in the spectra as the DCM concentration increases. Both titrations show a smooth transition from the ion-pair to free dye as the DCM concentration increases.

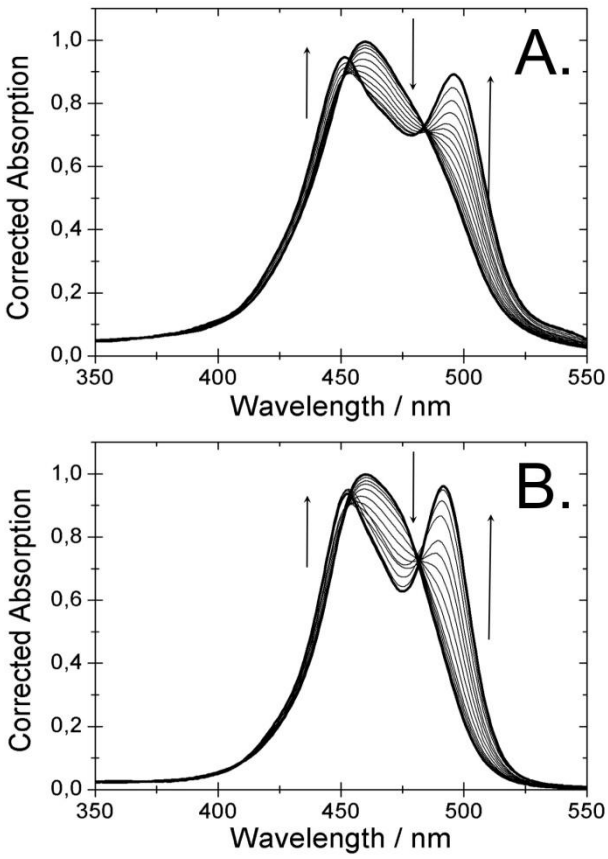

Figure S4. Titration of ATOTA·Cl (A.) and ATOTA·PF_6 (B.) in MCH with increasing amounts of benzene. The titration starts in pure MCH and ends in approximately 60 volume percent benzene. The two extreme spectra are shown in bold. The arrows point out the change in the spectra as the benzene concentration increases. Both titrations show a smooth transition from the ion-pair dimer to free ion-pairs as the benzene concentration increases.

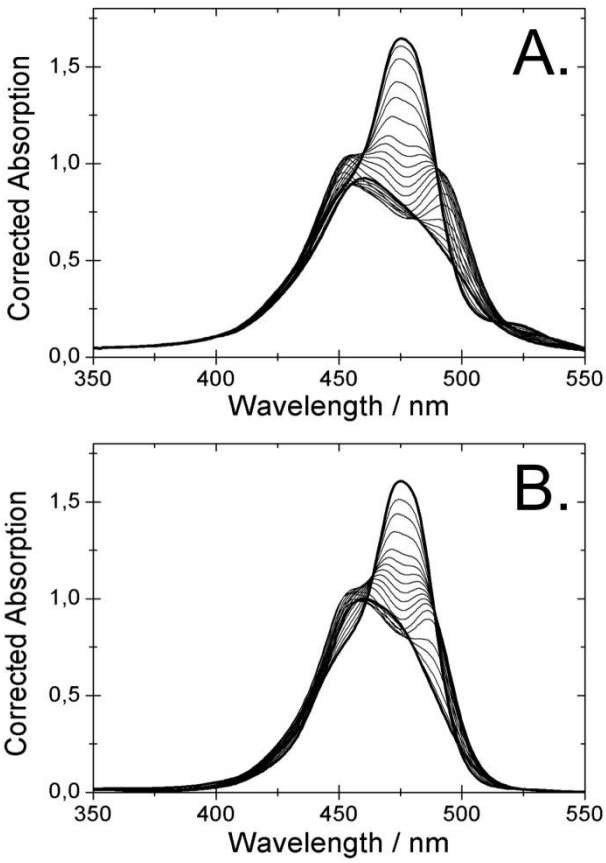

Figure S5. Titration of ATOTA·Cl (A.) and ATOTA·PF_6 (B.) in MCH with increasing amounts of DCM. The titration starts in pure MCH and ends in approximately 60 volume percent DCM. The two extreme spectra are shown in bold. Both titrations show a transition from dimers of ion-pairs via free ion-pairs to free dyes as the DCM concentration increases.

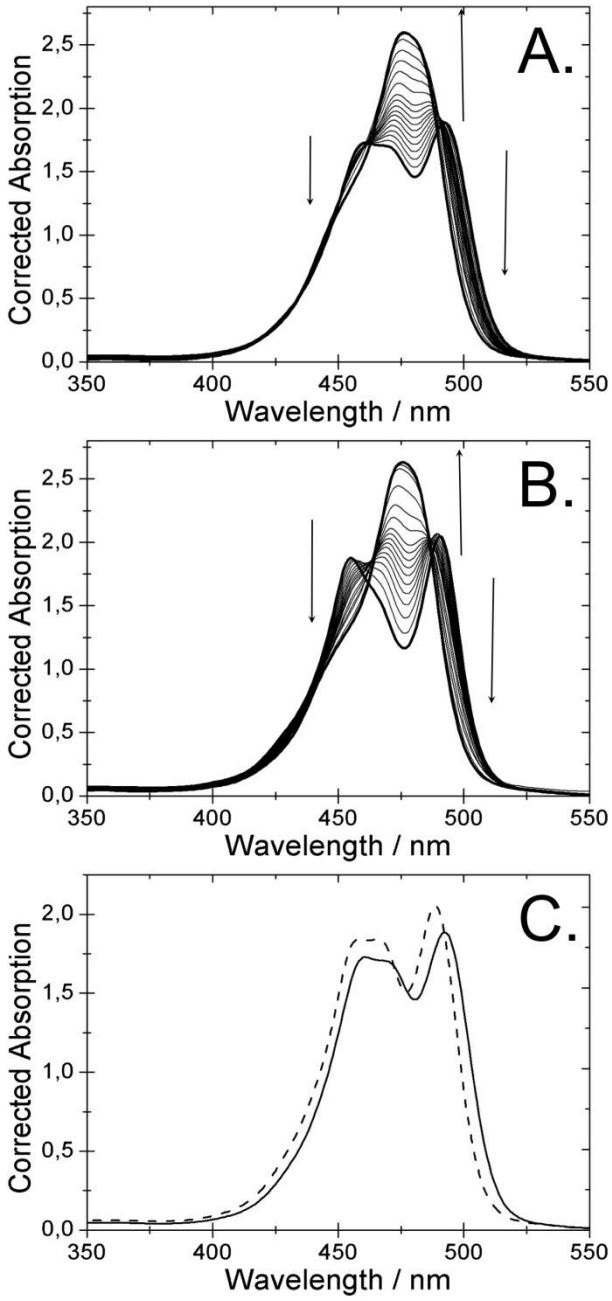

Figure S6. Titration of ATOTA·TT in benzene (A.) and MCH (B.) with increasing amounts of DCM. The titration starts in pure benzene/MCH and ends in approximately 60 volume percent DCM, the two extreme spectra are shown in bold. The arrows point out the change in the spectra as the DCM concentration increases. The spectra in pure benzene (solid line) and in a 13:87 volume percent mixture of DCM and MCH (dashed line) are shown in C. The spectra imply that the shoulder seen in pure benzene is due to an equilibrium between the ion pair and free dye and we can extract the spectrum of the ion pair alone in benzene by using the data in MCH-series.

Basis set analysis

Method: CAM-B3LYP

ATOTA$^+$

Vacuum	S_1 eV	$f(S_1)$	S_2 eV	$f(S_2)$	S_2-S_1 eV
6-31G	3.3380	0.7760	3.3432	0.7751	0.0052
6-31+G*	3.3154	0.7723	3.3226	0.7702	0.0072
6-31++G**	3.3154	0.7728	3.3220	0.7710	0.0066
6-311G	3.3194	0.7845	3.3240	0.7832	0.0046
6-311+G*	3.3038	0.7702	3.3103	0.7693	0.0065
6-311++G**	3.3053	0.7705	3.3116	0.7696	0.0063

Dichloromethane	S_1 eV	$f(S_1)$	S_2 eV	$f(S_2)$	S_2-S_1 eV
6-31G	3.2733	0.9376	3.2771	0.9348	0.0038
6-31+G*	3.2520	0.9436	3.2554	0.9458	0.0034
6-31++G**	3.2517	0.9477	3.2546	0.9482	0.0029
6-311G	3.2530	0.9544	3.2567	0.9507	0.0037
6-311+G*	3.2404	0.9445	3.2431	0.9463	0.0027
6-311++G**	3.2416	0.9487	3.2442	0.9479	0.0026

ATOTA·Cl

Vacuum	S_1 eV	$f(S_1)$	S_2 eV	$f(S_2)$	S_2-S_1 eV
6-31G	3.1212	0.7219	3.5567	0.5698	0.4355
6-31+G*	3.1188	0.7091	3.5245	0.5667	0.4057
6-31++G**	3.1180	0.7073	3.5248	0.5692	0.4068
6-311G	3.1194	0.7314	3.5375	0.6059	0.4180
6-311+G*	3.1088	0.7096	3.5108	0.5632	0.4020
6-311++G**	3.1095	0.7074	3.5127	0.5649	0.4032

Benzene (cavity 18 Bohr)	S_1 eV	$f(S_1)$	S_2 eV	$f(S_2)$	S_2-S_1 eV
6-31G	3.1313	0.8064	3.5115	0.7250	0.3802
6-31+G*	3.1356	0.7795	3.4796	0.7280	0.3441
6-31++G**	3.1356	0.7766	3.4795	0.7315	0.3440
6-311G	3.1319	0.8113	3.4873	0.7554	0.3554
6-311+G*	3.1242	0.7828	3.4663	0.7265	0.3421
6-311++G**	3.1256	0.7799	3.4678	0.7291	0.3421

ATOTA·BF_4

Vacuum	S_1 eV	$f(S_1)$	S_2 eV	$f(S_2)$	S_2-S_1 eV
6-31G	3.2127	0.7278	3.5199	0.6758	0.3072
6-31+G*	3.1995	0.7277	3.4848	0.6582	0.2853
6-31++G**	3.1983	0.7288	3.4849	0.6615	0.2866
6-311G	3.1942	0.7369	3.5007	0.6926	0.3065
6-311+G*	3.1881	0.7277	3.4712	0.6531	0.2831
6-311++G**	3.1886	0.7284	3.4730	0.6563	0.2844

Benzene (cavity 18 Bohr)	S_1 eV	$f(S_1)$	S_2 eV	$f(S_2)$	S_2-S_1 eV
6-31G	3.2139	0.8019	3.4648	0.8110	0.2509
6-31+G*	3.2002	0.8082	3.4314	0.8058	0.2312
6-31++G**	3.1990	0.8105	3.4313	0.8086	0.2323
6-311G	3.1951	0.8149	3.4437	0.8273	0.2486
6-311+G*	3.1885	0.8089	3.4182	0.8028	0.2298
6-311++G**	3.1890	0.8108	3.4197	0.8054	0.2307

ATOTA·PF_6

Vacuum	S_1 eV	$f(S_1)$	S_2 eV	$f(S_2)$	S_2-S_1 eV
6-31G	3.2188	0.7497	3.5215	0.7209	0.3026
6-31+G*	3.2003	0.7478	3.4907	0.7069	0.2905
6-31++G**	3.2001	0.7484	3.4911	0.7105	0.2910
6-311G	3.2012	0.7596	3.5020	0.7318	0.3008
6-311+G*	3.1900	0.7474	3.4780	0.7053	0.2881
6-311++G**	3.1912	0.7478	3.4797	0.7055	0.2886

Benzene (cavity 18 Bohr)	S_1 eV	$f(S_1)$	S_2 eV	$f(S_2)$	S_2-S_1 eV
6-31G	3.2282	0.8206	3.4458	0.8566	0.2177
6-31+G*	3.2091	0.8251	3.4170	0.8588	0.2079
6-31++G**	3.2090	0.8267	3.4172	0.8608	0.2082
6-311G	3.2104	0.8345	3.4244	0.8719	0.2140
6-311+G*	3.1985	0.8250	3.4046	0.8559	0.2061
6-311++G**	3.1998	0.8263	3.4061	0.8571	0.2064

ATOTA·TT

Vacuum	S_1 eV	$f(S_1)$	S_2 eV	$f(S_2)$	S_2-S_1 eV
6-31+G*	3.1137	0.662	3.4262	0.6973	0.3125

Benzene (cavity 24 Bohr)	S_1 eV	$f(S_1)$	S_2 eV	$f(S_2)$	S_2-S_1 eV
6-31+G*	3.1405	0.735	3.3393	0.893	0.1988

Molecule coordinates

Method: B3LY Basis set: 6-31+G*

ATOTA^{+}

Imaginary Vibration freq.: 0

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ATOTA·Cl

Imaginary Vibration freq.: 0

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C	-0.34443600	0.01416900	-0.11687000
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C	-3.53429500	-1.84513100	-0.08316900
C	-3.99527700	0.57462800	-0.21810400
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C	2.84348300	-5.53252900	0.47663400
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C	-6.34730200	-2.36006600	0.10541500
C	-6.41572200	-2.63846800	1.61321400
C	3.41037800	6.94117900	-0.43861700
C	2.94948900	5.50913200	-0.17448800
C	0.18606900	6.67334300	1.35813200
C	0.57187800	6.40083200	-0.10259700
C	5.29863900	-3.81845600	-1.18718200
C	-6.76558100	0.11005100	-0.26486500
C	-8.22085000	-0.23639200	-0.57813900
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O	-2.17478600	2.12100500	-0.24530900
O	2.37586600	0.55534600	-0.06238100
N	3.29022300	-4.14432400	0.31372000
N	-5.83106800	-1.02978000	-0.23864000
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Cl	6.02055500	-0.68690000	0.72244900

ATOTA·BF_4

Imaginary Vibration freq.: 0

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C	-2.85985300	-1.33435600	0.08351200
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C	-4.99972200	-0.21413700	0.36153200
C	-0.84796000	-0.01779200	-0.22929400
C	-0.73120200	-2.43714400	-0.15253800
C	-0.10368700	-1.18634100	-0.29855600
C	0.01327800	-3.59584500	-0.15407400
C	-0.96505700	2.40423500	-0.18180400
C	-0.21906300	1.21829300	-0.31357000
C	1.18397300	1.27446600	-0.45197900
C	1.29935500	-1.11050600	-0.44425400
C	1.44425100	-3.51874200	-0.30855400
C	2.07413600	-2.24403700	-0.45263700
C	-0.33667500	3.62875600	-0.19643700
C	1.84746800	2.48156400	-0.45885800
C	-7.17928100	0.93823700	0.63362000
C	-7.55001700	1.53091800	-0.73360200
C	-7.04966000	-1.56507000	0.71607000
C	1.09497600	3.69008500	-0.34330000
C	-7.41366900	-2.24967600	-0.60931000
C	4.24561200	-4.27617900	1.12762600
C	1.54861900	-5.95244500	-0.04331000
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C	1.04105800	6.13657400	-0.01815300
C	0.87608900	6.35232900	1.49306600
C	3.22641700	4.90173900	-0.43512200
C	3.87344600	6.26407700	-0.67380900
C	3.67797800	-4.56687600	-0.26641700
O	-2.34418900	2.32663700	-0.02336900
O	1.89696700	0.11556900	-0.56663300
O	-2.11091000	-2.49062000	0.01008100
N	-6.35852300	-0.27755200	0.57823900
N	1.74453200	4.89965500	-0.37097900
N	2.20425100	-4.65890000	-0.30946900
H	-4.89347200	1.98410600	0.30485200
H	3.14615300	-2.10743500	-0.52071700
H	-0.49648200	-4.53813400	-0.01354500
H	-4.68210400	-2.39229500	0.33340600
H	2.92858000	2.44707300	-0.49799300
H	-0.93725500	4.51940000	-0.07767700
H	-8.09309500	0.68066500	1.17730600
H	-6.66810100	1.68819000	1.24811200
H	-8.15408300	0.82906400	-1.31799800
H	-6.66088100	1.78038100	-1.32146200
H	-7.96157400	-1.37790000	1.29146500
H	-6.43901400	-2.23213300	1.33440800
H	-8.11405100	-1.64051800	-1.19037500
H	-6.52853400	-2.42797800	-1.22843900
H	0.34448200	7.29273400	1.68418900
H	3.72443700	6.96468900	0.15469300
H	-8.13503000	2.44826800	-0.59480900
H	5.33952200	-4.24148800	1.07604400
H	-7.89119300	-3.21678700	-0.40996500
H	3.25469100	-7.23883700	0.47659300
H	4.07419500	-5.50805000	-0.64849100
H	4.00147000	-3.80055900	-0.97332500
H	3.95799800	-5.05555600	1.84442900
H	3.90936600	-3.30670500	1.50716700
H	1.13883500	-5.95442300	0.97925400
H	0.69729400	-6.04296900	-0.72766100
H	1.79440700	-8.07439800	-0.05862200
H	2.82012700	-7.26328600	-1.24918500
H	1.59422500	6.97055300	-0.45132500
H	0.06825400	6.14529600	-0.51816700
H	1.85102200	6.40651100	1.99029000
H	0.30904200	5.53749700	1.95569700
H	3.63488500	4.45621300	0.48256700
H	3.52025900	4.24398100	-1.25759700
H	4.95235700	6.10338300	-0.77284700
H	3.52224800	6.73189800	-1.60073300
B	5.07213300	-0.00270000	0.37909600
F	4.13200600	-0.26437800	1.40617300
F	6.37185200	-0.00160300	0.89300700
F	4.94587600	-1.02305500	-0.61396300
F	4.78104500	1.25872100	-0.21334300

ATOTA·PF_6

Imaginary Vibration freq.: 0

H	4.88907400	-4.45632100	0.91915900
H	3.55253600	-3.44798400	1.46495700
H	1.50209300	-6.86113500	-1.93734000
H	-0.11859900	-6.15427700	-1.84351200
H	1.76863200	-6.60545100	0.55439700
H	-0.31267800	7.66237200	0.91675000
H	-0.52473500	6.00468400	1.52076000
H	1.29444000	6.86654600	-0.81682500
H	-0.24753300	6.06940500	-1.01819700
H	3.18671500	5.75246800	-2.14714500
H	3.33319100	3.98420700	-2.04719800
H	-8.69222500	0.75199400	-0.53150000
H	-8.64432700	-1.30290900	-0.29817200
H	-7.18777900	-2.20058300	-0.65015100
H	-1.07291200	-4.54269100	-0.20300900
H	-5.23902500	-2.33067600	-0.08177900
H	2.47498000	2.42256100	-0.40571700
H	-1.38089900	4.53550600	-0.23979000
H	-5.39035700	2.04740600	-0.12709100
H	2.63228900	-2.17063700	-0.36157700
H	-8.17966400	-1.38289100	2.15689100
H	-6.64660800	-2.21824200	1.86421400
H	-7.27299500	1.72375700	-0.83433500
H	-8.45486100	1.06150300	1.93997400
H	-6.96126800	1.98286600	1.70450600
H	3.00185100	5.87004600	0.37098200
H	3.13073800	4.12921100	0.47929100
H	0.17382600	-5.90417200	0.68173200
H	3.41150900	-5.63574300	-0.70992700
H	3.42101200	-3.91447100	-1.02537900
H	1.04034100	6.81401100	1.68968300
H	4.58813600	5.01098800	-1.34399700
H	-8.50477800	2.62868200	1.11350400
H	-8.17989600	-3.01640200	1.46626800
H	0.21775800	-7.71125500	-1.05609700
H	3.52155900	-5.19982000	1.77902200
C	-4.76981300	-1.35900300	-0.14043900
C	-3.39172600	-1.29759000	-0.22214300
C	-2.73894600	-0.05499200	-0.28745000
C	-3.47564800	1.14089100	-0.25256100
C	-4.85511000	1.10958400	-0.17254600
C	-5.53239600	-0.14934000	-0.12860000
C	-1.34200400	-0.00854600	-0.35461800
C	-1.43268600	2.41525100	-0.33354800
C	-0.69249400	1.21902500	-0.38472200
C	-0.78969100	3.63290900	-0.31130000
C	-1.26669900	-2.43098100	-0.27730800
C	-0.61039900	-1.18757400	-0.35814700
C	0.80043100	-1.13155600	-0.40385500
C	0.71882700	1.25650200	-0.41299200
C	0.64900700	3.67210400	-0.33041500
C	1.39399800	2.45440600	-0.38873800
C	-0.54273700	-3.60113700	-0.24522200
C	1.55595000	-2.27847600	-0.36643800
C	0.89620600	-3.54339200	-0.27583600
C	-7.62084100	-1.47463200	0.04783700
C	-7.65426800	-2.05377600	1.46939100
C	-7.71706200	1.02595600	-0.11637000
C	-7.91644700	1.71205800	1.24276800
C	2.77778100	4.93997900	-0.16260800
C	3.50881200	4.92055300	-1.50909500
C	0.61059900	6.15347600	-0.34371700
C	0.17622000	6.68689900	1.02818100
C	1.03275600	-6.00368900	0.01060800
C	0.63301600	-6.72215900	-1.28472800
C	3.11165500	-4.66676700	-0.29593600
C	3.80218100	-4.42865200	1.05095200
O	-2.65477500	-2.46471700	-0.23054700
O	1.42339900	0.08589500	-0.47258700
O	-2.81966500	2.35564700	-0.28551000
N	-6.90758400	-0.19774800	-0.08159000
N	1.63756000	-4.68716300	-0.21120400
N	1.30974700	4.86700600	-0.28255400
P	5.08741500	0.00721200	0.52975400
F	6.44196500	0.20387300	-0.36201200
F	4.37179900	1.26385400	-0.28848900
F	5.76969400	-1.25249000	1.32858800
F	4.49465300	-1.04899300	-0.61004600
F	3.69877400	-0.19665400	1.40100000
F	5.64296800	1.05885600	1.65368100

ATOTA·TT

Imaginary Vibration freq.: 0

C	-6.61114600	-1.06331000	-1.66470500
C	-5.31291600	-0.93019000	-1.19360000
C	-4.75297700	0.35981900	-1.08497700
C	-5.47439300	1.51969300	-1.43258900
C	-6.77670900	1.39249600	-1.89832700
C	-7.33726900	0.09818600	-2.03717500
C	-3.43825500	0.49105000	-0.60537400
C	-3.62984100	2.89876100	-0.84361300
C	-2.87149200	1.76104800	-0.48380700
C	-3.06576300	4.15492500	-0.72579100
C	-3.30673700	-1.91898400	-0.38828500
C	-2.71222900	-0.63588700	-0.25451600
C	-1.38188600	-0.48093400	0.22304900
C	-1.54575900	1.87640500	-0.00293900
C	-1.72991000	4.28234900	-0.23942300
C	-0.97405000	3.13124500	0.11695100
C	-2.57957000	-3.03990300	-0.05799200
C	-0.64755700	-1.59641800	0.56246400
C	-9.43194400	-1.24806700	-2.22692000
C	-10.06853500	-1.11129700	-0.84608900
C	-1.23221600	-2.89304800	0.41415300
C	1.16257500	5.94748600	-0.89220300
C	-9.36815600	1.08969400	-3.15812700
C	-9.91261000	2.04621000	-2.09991600
C	-1.78017600	6.76957500	-0.66255200
C	-1.95286300	7.91808400	0.33538800
C	5.12336700	-3.62646700	-0.39197800
C	5.48616800	-4.96669800	-0.46831700
C	3.90985900	-3.16358900	-0.99303200
C	4.63637500	-5.85119900	-1.15577900
C	3.08747600	-4.04988700	-1.67779200
C	3.46646900	-5.40137600	-1.74983800
C	3.47418500	-0.39538800	2.03002400
C	6.94396300	-0.06967200	-1.29950200
C	7.28800000	0.12675300	0.07092800
C	7.78378400	0.38308300	-2.31124100
C	8.46939100	0.77349400	0.41775900
C	8.97391600	1.03432600	-1.94805600
C	2.77722500	-0.31253900	3.22907100
C	3.43389000	0.68572800	1.08921700
C	2.04352800	0.85668000	3.50172900
C	2.70625500	1.83371000	1.37466700
C	9.30920300	1.22524300	-0.61338800
C	2.01406500	1.90546800	2.59636100
C	1.01245000	-4.20630600	2.73529000
C	0.90139700	-3.95234200	1.23504400
C	-0.73209100	-5.83668600	-0.97383400
C	-1.02760300	-5.38335100	0.45295900
C	0.25942400	5.71420900	0.31803700
O	-4.60841900	-2.07230400	-0.84698200
O	4.13847700	0.47187400	-0.02579200
O	5.77460400	-0.70643000	-1.49731800
O	6.38803300	-0.35439500	0.94841500
O	3.66909000	-1.85514800	-0.82277500
O	4.21875700	-1.43510900	1.63885600
O	5.83467400	-2.67242600	0.22319500
O	-0.79912300	0.76761200	0.35273600
O	-4.93220800	2.79005900	-1.31428500
N	-8.60865700	-0.07723900	-2.63731300
N	-0.50690200	-4.02024800	0.74525800
N	-1.18092000	5.55367200	-0.03066900
H	0.06524100	3.22671900	0.49597200
H	-3.64844000	5.04677100	-1.00379500
H	-7.07470600	-2.05891400	-1.76073800
H	-7.37306000	2.29291100	-2.12235700
H	-10.64655606	-0.21169131	-0.80734298
H	0.39254400	-1.49044700	0.91917400
H	-3.01963200	-4.04638400	-0.15088500
H	-10.21105000	-1.39533800	-3.00288800
H	-8.78197400	-2.15225100	-2.26024900
H	-9.30094977	-1.07439323	-0.10154147
H	-10.20073900	0.68329200	-3.77000800
H	-8.70686900	1.63235100	-3.86569100
H	-10.46704979	1.49323025	-1.37073158
H	-9.09863807	2.55026189	-1.62212798
H	0.30949200	6.59570100	1.00022600
H	0.62170000	4.83653800	0.90820200
H	0.68742611	6.62992925	-1.56555636
H	1.33729037	5.01734763	-1.39141953
H	-1.11474200	7.07795600	-1.50561300
H	-2.76327000	6.51924100	-1.11473000
H	-2.81285858	8.49612367	0.06859641
H	-2.08273786	7.51890015	1.31960585
H	-0.57326900	-6.08241000	1.19446000
H	-2.12646300	-5.39831400	0.63513800
H	0.31946496	-5.76797384	-1.15932981
H	-1.25762657	-5.20960155	-1.66338273
H	1.50879000	-4.68414900	0.65673900
H	1.33259900	-2.95359700	0.98991900
H	1.85379357	-3.67301932	3.12598978
H	0.12024393	-3.87013861	3.22094400
H	1.14119912	-5.25387679	2.91112826
H	-1.05090007	-6.85035852	-1.09924854
H	2.09545109	6.35853621	-0.56711851
H	-1.08366069	8.54176935	0.31529012
H	-10.55369841	2.76546939	-2.56528851
H	-10.70427485	-1.95194672	-0.66158186
P	5.02754600	-1.08776600	0.06914000
Cl	7.41038800	0.16951800	-3.93051100
Cl	10.00553200	1.58965200	-3.15434800
Cl	10.74307200	2.00970700	-0.21835400
Cl	8.90397500	1.02077400	2.01644700
Cl	6.89575600	-5.54052900	0.22792900
Cl	5.05439300	-7.47569700	-1.26064900
Cl	2.48217100	-6.48467200	-2.58308500

Cl	1.67748400	-3.54734700	-2.44129600
Cl	2.80736400	-1.55569100	4.35461100
Cl	1.20012400	0.97665200	4.95108000
Cl	1.13906700	3.30104900	2.95842300
Cl	2.64216000	3.12941900	0.3074520

Excitation energy calculation

Method: CAM-B3LYP Basis set: 6-311++G** Solvent: Benzene

Ion	S_1 eV	$f(S_1)$	S_1(exp) eV	S_2 eV	$f(S_2)$	S_2-S_1 eV	ΔS_1 (vs experiment) cm^{-1}
none	3.24	0.95	2.64	0.95	0.76960	0.00630	5145
Cl^-	3.13	0.78	2.48	0.73	0.7423	0.0116	5090
BF_4^-	3.18	0.81	2.51	0.81	0.76410	0.01498	5376
PF_6^-	3.20	0.83	2.52	0.86	0.7581	0.00626	5508
ΔTT^-	3.16	0.74	2.52	0.88	0.73680	0.01106	5196

Assigned transitions and transition dipole moments

Method: CAM-B3LYP Basis set: 6-311++G**

ATOTA$^+$

Vacuum

	x	y	z	Length
$S_0 \rightarrow S_1$	0.8883	-2.9524	-0.0921	3.0845
$S_0 \rightarrow S_2$	-2.9496	-0.8860	-0.0011	3.0798

Benzene

x	y	z	Length
-0.9780	3.0571	0.0951	3.2111
-3.0576	-0.9745	-0.0029	3.2091

DCM

	x	y	z	Length
$S_0 \rightarrow S_1$	-1.1165	3.1291	0.0976	3.3238
$S_0 \rightarrow S_2$	-3.1332	-1.1114	-0.0062	3.3245

ATOTA·Cl

Vacuum

	x	y	z	Length
$S_0 \rightarrow S_1$	1.5019	-2.6511	0.0491	3.0474
$S_0 \rightarrow S_2$	-2.3795	-0.9496	0.0004	2.5620

Benzene

x	y	z	Length
1.6045	-2.7582	0.0485	3.1913
-2.6448	-1.2597	0.0033	2.9295

ATOTA·BF_4

Vacuum

	x	y	z	Length
$S_0 \rightarrow S_1$	0.3403	-3.0345	0.0175	3.0536
$S_0 \rightarrow S_2$	2.7648	0.2120	-0.1574	2.7774

Benzene

x	y	z	Length
-0.3888	3.1980	-0.0148	3.2216
-3.0806	-0.3059	0.1706	3.1004

ATOTA·PF_6

Vacuum

	x	y	z	Length
$S_0 \rightarrow S_1$	-0.2730	3.0805	-0.0283	3.0927
$S_0 \rightarrow S_2$	-2.8648	-0.2276	0.1286	2.8767

Benzene

x	y	z	Length
0.3336	-3.2294	0.0248	3.2467
3.1878	0.2952	-0.1482	3.2049

ATOTA·TT

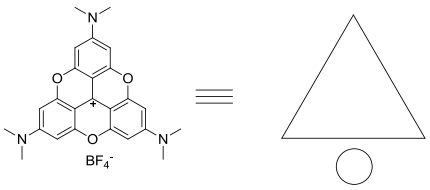
Vacuum

Transition	x	y	z	Length
$S_0 \rightarrow S_1$	0.9129	-2.7713	0.4116	2.94668
$S_0 \rightarrow S_2$	-2.6914	-0.6805	-0.7751	2.88227

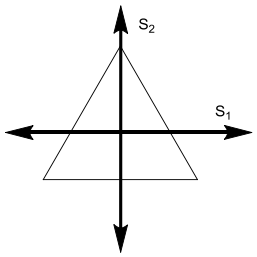
Benzene

x	y	z	Length
-1.2180	2.7965	-0.4998	3.09091
-3.0548	-0.9131	-0.8646	3.30350

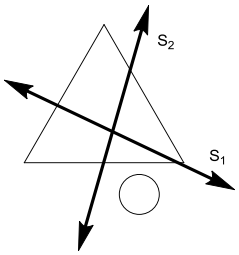
Orientation of transition dipole moments for the ion pairs in benzene



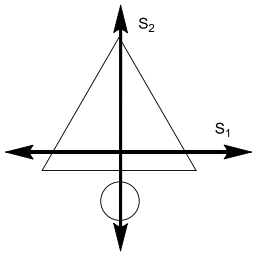
ATOTA$^+$



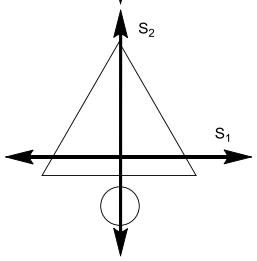
ATOTA·Cl



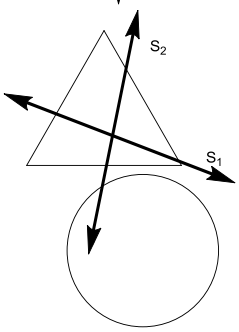
ATOTA·BF_4



ATOTA·PF_6



ATOTA·TT



Geometry effect upon ion-pair formation

The excitation energies are calculated for the ion pair geometries of $ATOTA^+$, with anions removed. The differences are in all cases very small. Thus, no significant change of the geometry of the cation happens upon ion-pair formation. Method: CAM-B3LYP, Basis set: 6-311++G**

Ion	S_1 eV	$f(S_1)$	S_2 eV	$f(S_2)$	S_2-S_1 eV	ΔS_1 (vs. $ATOTA^+$) eV
none	3.30528	0.77050	3.31158	0.76960	0.00630	0
Cl^-	3.2997	0.7872	3.3113	0.7423	0.0116	0.00560
BF_4^-	3.30083	0.75860	3.31581	0.76410	0.01498	0.00445
PF_6^-	3.3086	0.7785	3.3148	0.7581	0.00626	-0.00329
ΔTT^-	3.24300	0.77670	3.25407	0.73680	0.01106	0.06228

Solvent cavity calculation

The size of the cavity was tested on $ATOTA{\cdot}BF_4$, a cavity of 18 Bohr was found to be best suited. Method: CAM-B3LYP, Basis set: 6-311++G**

cavity	S_1 eV	$f(S_1)$	S_2 eV	$f(S_2)$	S_2-S_1 eV	ΔS_1 (vs vacuum) eV
vacuum	3.1886	0.7284	3.4730	0.6563	0.2844	0
16	3.2126	0.8496	3.4163	0.9126	0.2037	-0.0240
17	3.2132	0.8207	3.4471	0.8492	0.2339	-0.0246
18	3.2139	0.8019	3.4648	0.8110	0.2509	-0.0253
19	3.2144	0.7885	3.4765	0.7851	0.2620	-0.0258
20	3.2147	0.7784	3.4847	0.7662	0.2699	-0.0261

Absorbance spectra in the lamellar liquid crystal

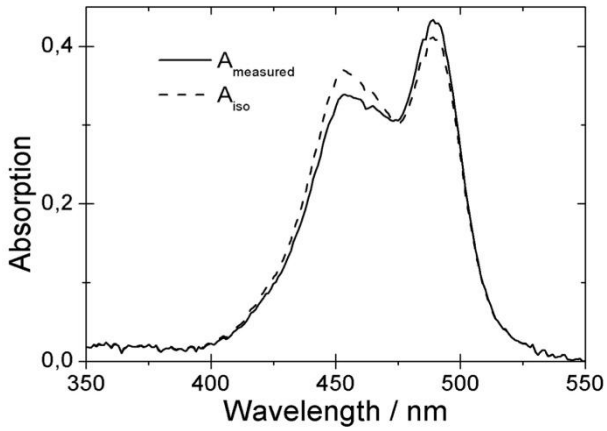


Figure S7. The measured (solid line) and the corrected (dashed line) absorption spectrum of R_2-ATOTA·PF_6 oriented in the lamellar liquid crystal.

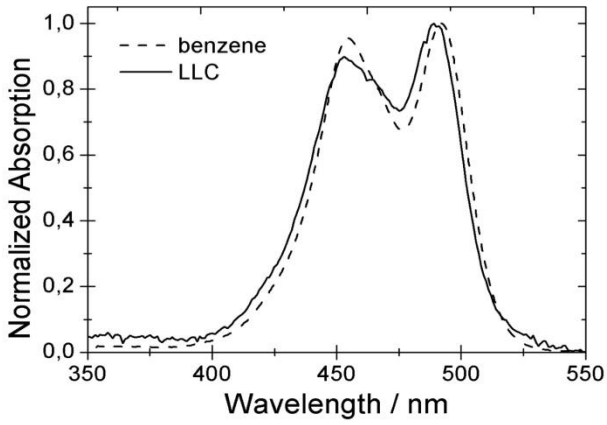


Figure S8. Absorption spectra of R_2-ATOTA·PF_6 in the lamellar liquid crystal (solid line) and of ATOTA·PF_6 in benzene (dashed line).

Analysis of LD spectra

The macroscopic orientation direction *Z* of the lamellar liquid crystals is taken to be the normal of the quartz-plates used to induce such aligned samples in the spectroscopic cell (See Figure SY). In order to define the direction of the two transition moments within the $ATOTA^+$ framework we introduce a molecular orientation axis *z* which corresponds to the line drawn from the corner modified with the decyl chains and runs perpendicularly to the opposing triangle edge. The direction of the two transition moments (at 488 and 450 nm respectively) is then defined by their corresponding angles (α_{488} and α_{450}) relative to the *z* axis. From symmetry considerations and MO calculations we predict $\alpha_{488} = 90^o$ and $\alpha_{450} = 0^o$.

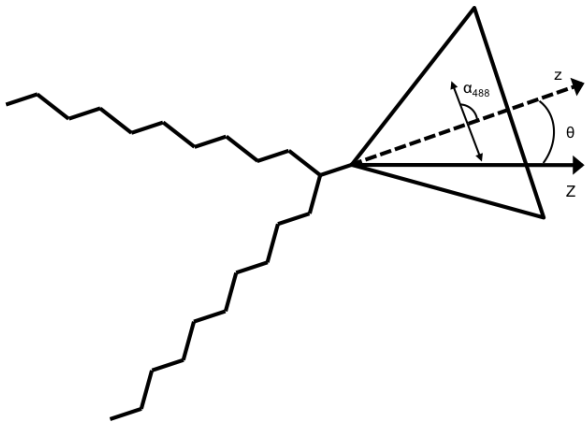


Figure S9. Geometry of the experimental set up. The macroscopic orientation axis of the sample is denoted *Z*, the normal to the bilayer surface. The orientation axis of the $ATOTA^+$ ion (the solid triangle) is denoted *z*. The degree of $ATOTA^+$ orientation is quantified by the angle θ between *Z* and *z*. The orientation of the transition moments within the $ATOTA^+$ framework is given by the angle α_i between transition moment *i* and the molecular axis *z* (as exemplified by $\alpha_{488} = 90^o$).

To calculate the angle between the two transition moments we use the reduced linear dichroism (LD^r)

$$LD^r = LD/A_{iso} = 3*S*(3*cos^2\alpha_i - 1)/2 \qquad \text{(S1 = E1)}$$

where the experimental values of LD and A_{iso} at the two relevant wavelengths (i=488 and i=450) are given in Table S1. The orientation factor

$$S = <3*cos^2\theta - 1>/2 \qquad \text{(S2)}$$

quantifies the average orientation of the $ATOTA^+$ ions in terms of the angle θ between the macroscopic (Z) and molecular (z) orientation axes. The average indicated by brackets in (S2) runs over all dye molecules and all lamellar layers in the sample. Equation (S1) assumes that the orientation distribution of *z* is cylindrically symmetric around *Z*, and the orientation factor *S* has the same value for both transitions. Using the measured LD^r-value at 488 nm and the fact that $\alpha_{488} = 90^o$ in our molecular coordinate system we use equation (S1) to calculate *S*. Using this *S*-value and the LD^r-value at 450 nm equation (S1) gives $\alpha_{450} = 15^o$ (cos $\alpha_{450} = 0.97$), which should be compared to the predicted value 0° (cos $\alpha_{450} = 1$).

Table S1. Spectroscopic values used for calculating angles of transition moments.

	A_m [a]	A_{iso} [b]	LD	LD^r [c]
				0.0527
450 nm	0.323	0.357	0.0188	
488 nm	0.432	0.410	-0.0120	-0.0293

a. Measured absorbance in the oriented sample.
b. Absorbance of corresponding isotropic sample calculated from (E2).
c. Reduced linear dichroism $LD^r = LD/A_{iso}$.

$$S_{488} = LD/A_{iso} * 2 / (3*(3*\cos^2 \alpha_{488} - 1))$$

$$S_{488} = -0.0120/0.410 * 2 / (3*(3*\cos^2 90 - 1))$$

$$S_{488} = -0.0120/0.410 * 2 / (3*(0 - 1))$$

$$S_{488} = 0.0120/0.410 * 2 / 3$$

S is equal for both transitions and S_{488} can thus be used to calculate the angle (α_{450}) for the transition at 450 nm.

$$3*\cos^2 \alpha_{450} - 1 = (LD/A_{iso}) / S_{488} * 2 / 3$$

$$\cos^2 \alpha_{450} = (0.0188/0.357) / (0.0120/0.410 * 2/3) *2/3 +1) / 3$$

$$\cos^2 \alpha_{450} = (0.0188/0.357) / (0.0120/0.410) + 1) / 3$$

$$\cos^2 \alpha_{450} = 0.933$$

$$\alpha_{450} = 15°$$

References

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