Supporting Information
Fluorescent labelling to investigate nanopatterning processes in extreme-ultraviolet lithography

Lianjia Wu,[*,†] Michiel F. Hilbers,[‡] Olivier Lugier,[†] Neha Thakur,[†] Michaela Vockenhuber,[¶] Yasin Ekinci,[¶] Albert M. Brouwer,[†,‡] and Sonia Castellanos[*,†]

†*Advanced Research Center for Nanolithography, Science Park 106, 1098XG Amsterdam, The Netherlands*

‡*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, PO Box 94157, 1090 GD Amsterdam, The Netherlands*

¶*Laboratory of Micro and Nanotechnology, Paul Scherrer Institute, Forschungsstrasse 111, 5232 Villigen, Switzerland*

E-mail: l.wu@arcnl.nl; s.castellanos@arcnl.nl

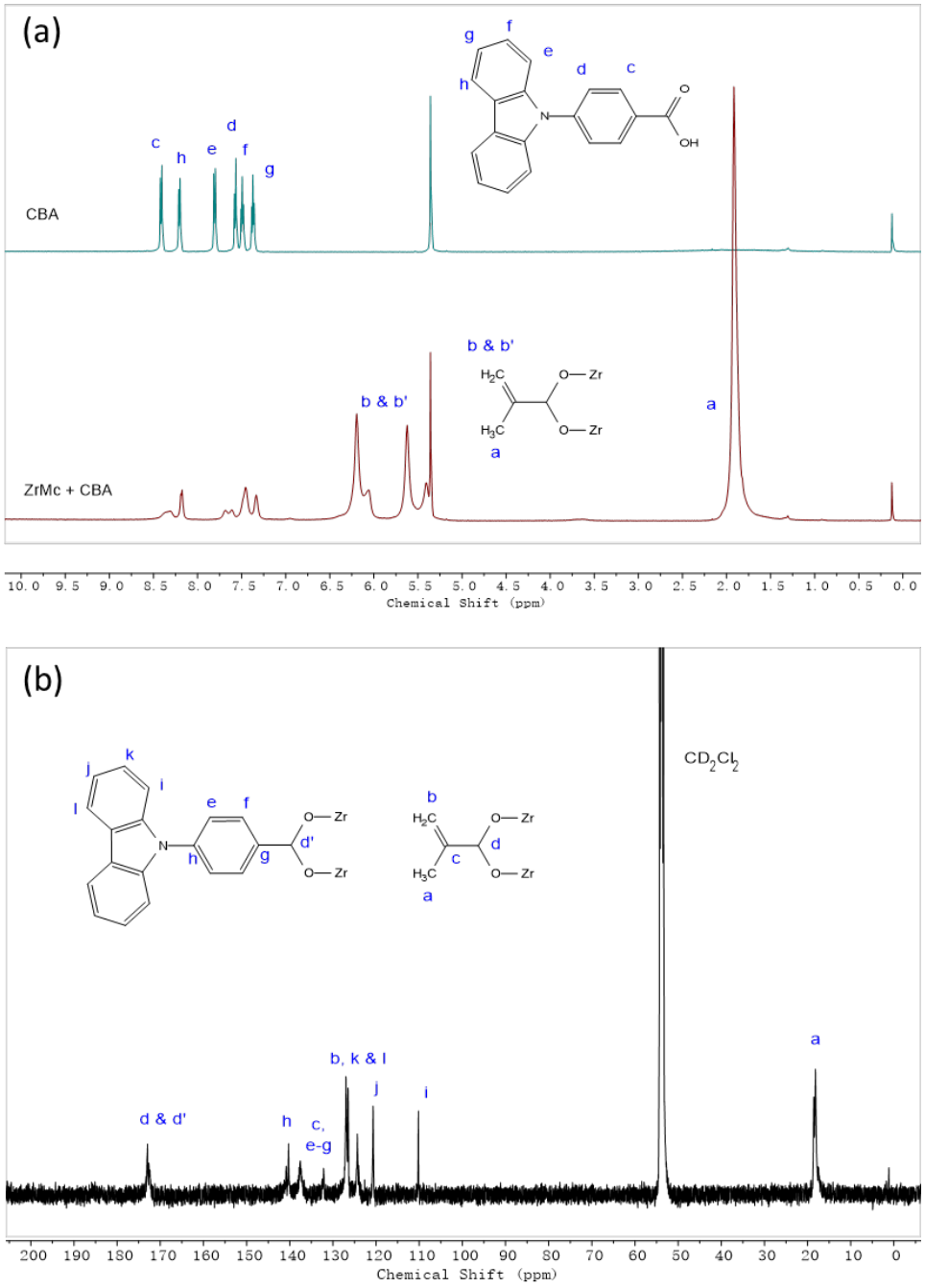


Figure S1: (a) ^{1}H and (b) ^{13}C NMR of ZrMc with one molar equivalent CBA in CD_2Cl_2.

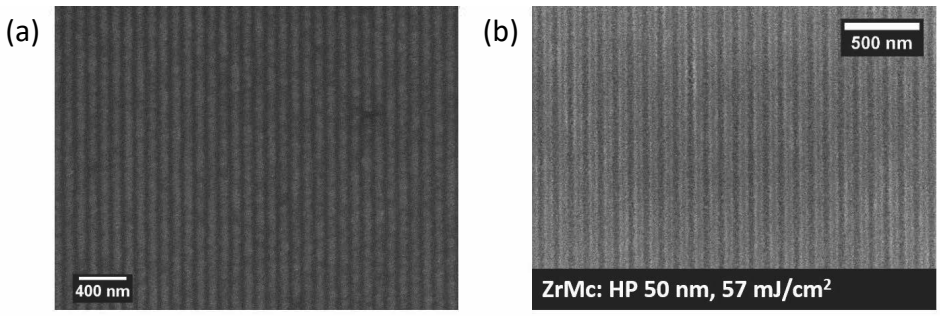
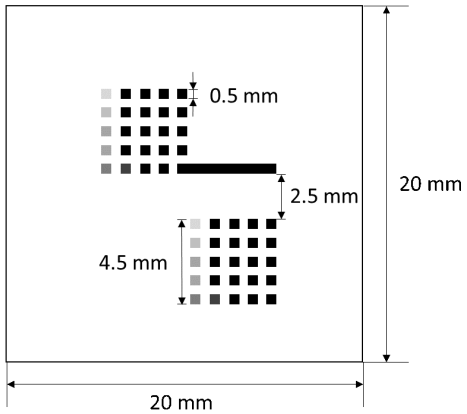


Figure S2: Top-down SEM images of line-space patterns of (a) ZrMc-CB, with EUV dose 90 mJ/cm^2 for 50 nm half-pitch and (b) the ZrMc precursor.



Scheme S1: Exposure scheme of the sample for fluorescence intensity and correlating film thickness measurement.Repetition of the highest dose in a row was designed to distinguish between up/bottom sides and low-/high-dose areas. An arrow marker was later written before microscopic characterization with a fluorescent marker pen for surface focus and location indication under the microscope.

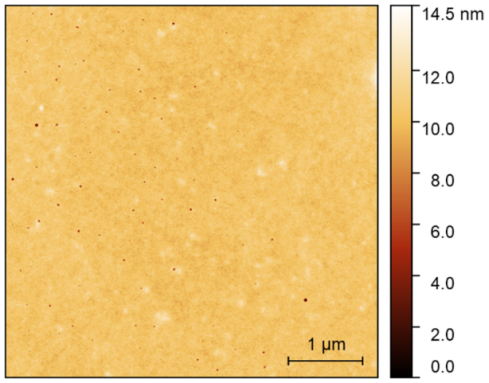


Figure S3: AFM image of the surface of spin-coated ZrMc-CB thin film with RMS roughness (S_q) of 0.480 nm and mean roughness (S_a) of 0.362 nm.

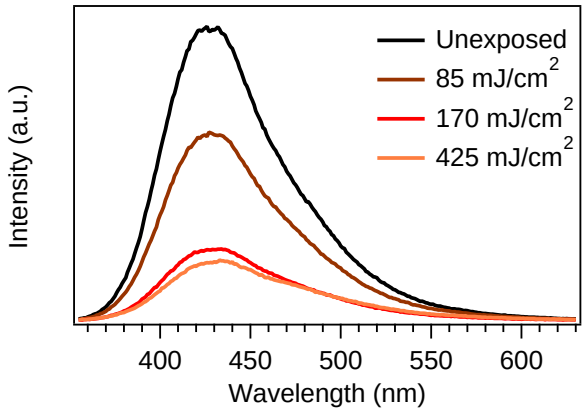


Figure S4: Fluorescence spectra of pristine and EUV-exposed ZrMc-CB films on quartz (λ_{exc} = 345 nm).

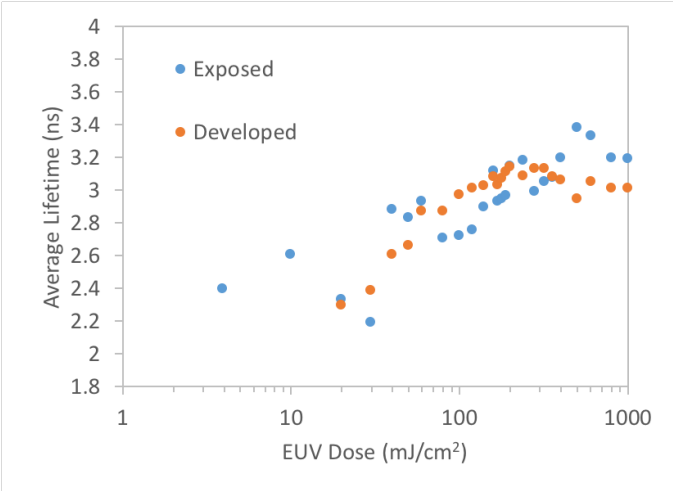


Figure S5: Average fluorescence lifetimes of on an exposed sample that was not developed ("exposed") and an exposed sample after development ("developed")

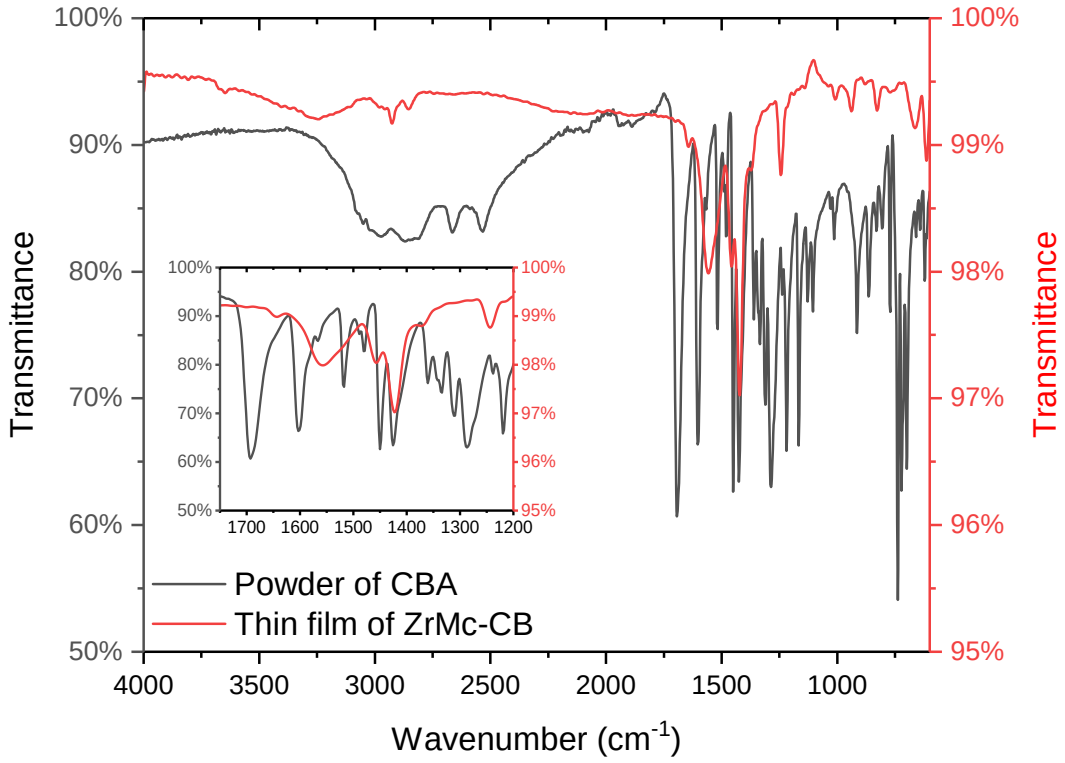


Figure S6: ATR-FTIR spectrum of the CBA ligand as a powder and FTIR transmission spectrum of a non-exposed ZrMc-CB thin film deposited on Si

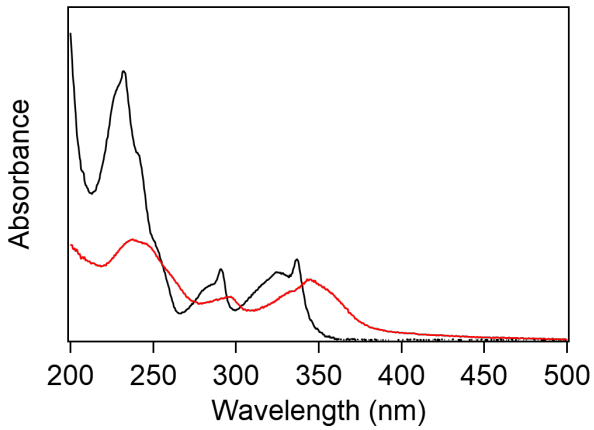


Figure S7: UV absorption of CBA drop-casted film (in red) and solution in n-pentane (in black), 1:1 (v/v) diluted from a saturated solution.

Table S1: Optimized geometry of ZrMc in Cartesian coordinates

Atom	X	Y	Z	Atom	X	Y	Z
Zr	1.71444	1.53242	-1.09593	C	5.86453	2.18439	2.761
Zr	-1.19053	2.00014	0.85324	H	6.84356	2.57939	3.0463
Zr	1.36129	-1.99853	-0.82657	H	5.32192	1.57484	3.48615
Zr	-1.30209	-0.05595	-2.09049	C	4.79771	-3.15517	1.97417
Zr	1.47161	0.00917	2.11126	C	5.36831	-2.84671	3.14913
Zr	-1.54781	-1.56233	1.1668	H	6.2661	-3.36591	3.49603
O	1.02818	1.51406	3.67588	H	4.94564	-2.06536	3.78374
O	-0.73477	2.68872	2.93298	C	-5.53111	-1.61423	2.40625
O	0.60096	-4.03584	-0.37295	C	-5.99844	-0.70347	3.27451
O	-1.30013	-3.74243	0.78443	H	-7.03596	-0.7273	3.61978
O	1.30059	2.22034	-3.16913	H	-5.34321	0.08458	3.65273
O	-0.66218	1.2934	-3.74395	C	-4.94748	3.75017	0.37931
O	-3.16123	2.68615	1.62704	C	-5.69283	3.90051	1.48554
O	3.37969	1.17398	2.07575	H	-6.68149	4.36663	1.44532
O	-2.87597	2.94685	-0.5169	H	-5.32167	3.55665	2.45337
O	3.53304	2.1442	0.0552	C	-5.27224	-0.64877	-3.23891
O	1.35906	3.74361	-0.94477	C	-5.88049	0.36842	-3.8695
O	-0.47431	4.02183	0.31989	H	-6.91413	0.28496	-4.21725
O	1.05922	1.97916	1.04032	H	-5.34759	1.30476	-4.04947
O	-0.38258	1.44716	-0.97628	C	-0.48075	-2.31942	5.54054
O	-3.22323	0.62184	-2.99223	C	-1.53987	-3.08721	5.84083
O	3.45774	0.61043	-2.16242	H	-1.70352	-3.45204	6.85868
O	-3.25956	-1.39832	-2.17611	H	-2.26437	-3.36127	5.07162
O	3.22544	-1.61817	-1.99639	C	6.0196	3.26374	0.49565
O	0.77461	-2.88173	-2.79575	H	6.17099	2.67819	-0.42537
O	-0.91185	-1.63617	-3.59562	H	5.39924	4.1278	0.20835
O	0.93939	-0.27134	-2.25302	H	6.99508	3.62932	0.84726
O	-0.6787	-1.49257	-0.73044	C	-1.18769	4.01369	5.30912
O	-3.64657	-2.34124	1.10712	H	-1.09543	4.83479	4.5801
O	3.04708	-2.76078	0.43662	H	-2.15139	3.52504	5.0949

Continued on next page

Table S1 – Continued from previous page

Atom	X	Y	Z	Atom	X	Y	Z
O	-3.31549	-0.641	2.42794	H	-1.2185	4.44	6.3222
O	3.10382	-1.50072	2.29583	C	5.31773	-4.21176	1.03781
O	0.7311	-1.14738	3.88362	H	4.55524	-4.98504	0.8517
O	-1.16979	-2.16175	3.25771	H	5.5609	-3.77824	0.05444
O	1.84307	-0.18291	0.07129	H	6.2182	-4.69293	1.44595
O	-2.42986	0.23225	-0.06143	C	5.89787	0.5177	-3.45513
O	0.66284	-1.9787	1.34191	H	5.27685	1.12961	-4.12885
O	-0.5866	0.19614	1.7043	H	6.10575	1.14871	-2.57615
C	0.09383	2.35898	3.83145	H	6.84756	0.28818	-3.95933
C	-0.47046	-4.46439	0.15892	C	0.558	-1.8883	6.53983
C	0.30834	2.07828	-3.95012	H	1.56161	-2.23063	6.24033
C	-3.60512	3.10362	0.49873	H	0.61177	-0.78924	6.59683
C	3.98665	1.86975	1.20871	H	0.3322	-2.28507	7.54006
C	0.46534	4.46494	-0.4087	C	-1.44192	-3.27186	-5.75548
C	-3.85859	-0.47169	-2.78455	H	-2.40804	-3.24494	-5.22653
C	3.85874	-0.57857	-2.34868	H	-1.31245	-2.27583	-6.20853
C	-0.13521	-2.6397	-3.64236	H	-1.49661	-4.02172	-6.55771
C	-4.10212	-1.51496	1.97456	C	0.27692	-6.76172	-0.70494
C	3.56196	-2.4113	1.54182	H	0.40308	-6.39583	-1.73656
C	-0.30114	-1.84119	4.12602	H	1.26748	-6.68518	-0.22821
H	0.89701	-2.75632	1.86246	H	-0.0187	-7.82029	-0.73777
H	1.28573	-0.3777	-3.14695	C	-6.34478	-2.73732	1.8236
H	-3.39091	0.32984	-0.08223	H	-6.3634	-2.68116	0.72331
H	1.45122	2.75732	1.4541	H	-5.89933	-3.71452	2.07048
C	-0.74425	-5.93815	0.03165	H	-7.37845	-2.71444	2.19782
C	-1.87426	-6.43491	0.55883	C	-5.36165	4.18427	-0.99992
H	-2.11434	-7.49908	0.48141	H	-4.64496	4.91196	-1.41335
H	-2.58139	-5.779	1.07076	H	-5.36104	3.32969	-1.69558
C	-0.05138	3.03869	5.16679	H	-6.36349	4.63723	-0.98971
C	0.81886	2.74754	6.14662	C	1.69403	6.43136	-1.50426
H	0.74388	3.22131	7.12942	H	2.66507	6.14199	-1.07132

Continued on next page

Table S1 – Continued from previous page

Atom	X	Y	Z	Atom	X	Y	Z
H	1.6237	2.02886	5.97955	H	1.65708	5.97194	-2.50499
C	0.55458	5.94742	-0.64926	H	1.66769	7.5248	-1.61572
C	-0.3689	6.75409	-0.10334	C	-5.90943	-1.97908	-2.94518
H	-0.33692	7.83627	-0.25752	H	-5.35269	-2.79597	-3.43208
H	-1.17583	6.34317	0.50643	H	-5.88097	-2.19778	-1.86557
C	-0.32024	-3.58075	-4.80201	H	-6.95301	-2.00567	-3.29018
C	0.50645	-4.63079	-4.92798	C	1.51708	3.77771	-5.4464
H	0.40352	-5.33582	-5.75755	H	1.64598	4.49857	-4.62319
H	1.30279	-4.80141	-4.20071	H	2.44362	3.18195	-5.47779
C	5.1794	-0.74188	-3.05443	H	1.42139	4.33217	-6.39101
C	5.64564	-1.97842	-3.28963	C	0.31692	2.90182	-5.20937
H	6.60004	-2.13613	-3.7997	C	-0.73469	2.82566	-6.04008
H	5.07656	-2.85558	-2.9752	H	-0.77126	3.41361	-6.96154
C	5.3387	2.43696	1.55234	H	-1.58056	2.17642	-5.80461

Table S2: Calculated molecular orbitals of ZrMc

	Orbital	E (eV)
343	LUMO+2	-1.376
342	LUMO+1	-1.394
341	LUMO	-1.727
340	HOMO	-7.139
339	HOMO-1	-7.164
338	HOMO-2	-7.182

Table S3: Calculated excitation energies and oscillator strengths for the first 10 excited states of ZrMc

Excited State 1	Singlet-A	4.8867 eV	253.72 nm	f=0.0005
328 → 341	0.46327			
329 → 341	0.32405			
330 → 341	-0.1211			
331 → 341	-0.15073			

Continued on next page

Table S3 – Continued from previous page

332 → 341	-0.15431			
334 → 341	-0.11179			
Excited State 2	Singlet-A	4.9362 eV	251.18 nm	f=0.0029
326 → 341	0.35971			
327 → 341	-0.19337			
331 → 341	-0.18747			
332 → 341	0.16438			
336 → 341	0.11015			
338 → 341	-0.13033			
339 → 341	-0.30167			
Excited State 3	Singlet-A	4.9413 eV	250.92 nm	f=0.0049
326 → 341	0.17093			
327 → 341	0.39531			
333 → 341	-0.18726			
334 → 341	0.18283			
335 → 341	-0.18898			
336 → 341	-0.15657			
340 → 341	0.19606			
Excited State 4	Singlet-A	4.9918 eV	248.38 nm	f=0.0025
320 → 346	-0.11021			
321 → 347	0.10783			
323 → 346	-0.14925			
324 → 347	-0.11211			
325 → 341	0.2051			
325 → 344	0.24231			
325 → 345	0.19403			
326 → 347	-0.12408			
327 → 346	-0.13664			
340 → 341	0.21743			
Excited State 5	Singlet-A	5.0125 eV	247.35 nm	f=0.0082
320 → 344	-0.10432			
320 → 345	-0.10502			

Continued on next page

Table S3 – Continued from previous page

322 → 346	-0.10072			
323 → 341	-0.14595			
323 → 344	-0.18561			
323 → 345	-0.13701			
323 → 346	0.11565			
325 → 346	0.20396			
325 → 350	0.11628			
327 → 344	-0.12291			
327 → 345	-0.13905			
339 → 341	-0.11014			
340 → 341	0.25964			
Excited State 6	Singlet-A	5.0163 eV	247.16 nm	f=0.0088
325 → 347	-0.11324			
335 → 341	0.14145			
336 → 341	0.22089			
337 → 341	-0.28634			
340 → 341	0.40277			
Excited State 7	Singlet-A	5.0192 eV	247.02 nm	f=0.0043
324 → 341	-0.14256			
324 → 344	-0.15483			
324 → 345	-0.11979			
324 → 346	-0.12156			
325 → 346	-0.11467			
325 → 347	0.14666			
325 → 349	-0.10677			
325 → 351	0.12643			
326 → 345	-0.11682			
327 → 345	0.10771			
335 → 341	0.10601			
336 → 341	0.11296			
340 → 341	0.16315			
Excited State 8	Singlet-A	5.0397 eV	246.01 nm	f=0.0107

Continued on next page

Table S3 – Continued from previous page

337 → 341	0.29396			
338 → 341	-0.35983			
339 → 341	0.37833			
340 → 341	0.20493			
Excited State 9	Singlet-A	5.0477 eV	245.62 nm	f=0.0028
327 → 341	-0.14424			
336 → 341	-0.19772			
337 → 341	0.42302			
338 → 341	0.23955			
339 → 341	-0.14382			
340 → 341	0.2512			
Excited State 10	Singlet-A	5.0596 eV	245.05 nm	f=0.0080
323 → 341	-0.12699			
326 → 341	0.1114			
330 → 341	0.13948			
331 → 341	-0.1762			
338 → 341	0.38126			
339 → 341	0.32215			

Table S4: Optimized geometry of ZrMc-CB in Cartesian coordinates

Atom	X	Y	Z	Atom	X	Y	Z
Zr	3.07456	1.64915	0.33361	C	-10.5375	1.36452	3.15047
Zr	3.01567	-1.719	-0.73022	C	-5.43938	-1.31484	-0.02002
Zr	-0.49013	1.55531	0.79197	C	-6.83134	-1.28582	-0.07504
Zr	1.56586	-0.82164	2.39652	C	5.72368	0.09253	-0.63731
Zr	0.93488	0.64648	-2.37626	C	3.76951	-3.19883	2.06164
Zr	-0.51597	-1.82114	-0.31052	C	3.76926	4.01201	-0.72006
O	2.59706	0.29849	-1.16784	C	-0.4803	1.13973	3.99492
O	3.41143	-0.44001	1.11545	C	-0.50673	-3.31891	2.58367
O	1.09855	2.32	-0.74179	C	-0.83752	4.21235	0.88481

Continued on next page

Table S4 – Continued from previous page

Atom	X	Y	Z	Atom	X	Y	Z
O	1.37349	-1.76482	0.5506	C	-1.46356	-1.26225	-3.37883
O	5.16328	1.11652	-0.13831	C	1.23943	-4.4042	-1.21819
O	5.13986	-1.01288	-0.84435	C	0.0806	2.82124	-3.68528
O	3.94172	-3.03308	0.81643	C	-3.21726	-0.17791	0.33077
O	3.68739	3.01559	-1.48745	C	3.72082	1.30623	3.50609
O	3.01788	-2.48052	2.78835	C	3.2663	-1.07392	-3.8762
O	3.45811	3.84754	0.51245	H	-0.43076	7.58691	1.67841
O	1.40942	1.04839	1.4436	H	0.87144	6.3924	1.37246
O	-0.5503	-0.5564	1.58485	H	-0.1576	6.20724	2.78605
O	-0.95704	1.68991	2.95391	H	-4.18473	-2.78807	-4.96798
O	0.35713	0.19049	3.98358	H	-4.09386	-2.32845	-3.24041
O	0.34506	-2.54607	3.11613	H	-3.02752	-3.58686	-3.86064
O	0.16345	3.73201	1.48043	H	-1.96139	5.39186	-4.86773
O	-0.96436	-3.18902	1.40759	H	-1.88461	4.78164	-3.18428
O	-1.59824	3.40658	0.2401	H	-2.48522	3.72845	-4.45976
O	-0.34553	0.21733	-0.7989	H	4.62672	7.39964	-0.61659
O	1.07584	-1.5596	-1.91827	H	5.02239	6.17667	0.62916
O	-0.58987	-0.37137	-3.61012	H	3.3396	6.60595	0.34198
O	-1.54541	-1.92316	-2.30025	H	4.71312	1.64243	6.84852
O	0.11897	-3.86106	-0.96946	H	4.53731	0.10301	5.95327
O	-0.70803	2.28426	-2.86216	H	3.11092	1.08703	6.27499
O	2.3501	-3.79556	-1.22329	H	-2.22088	3.12852	6.29225
O	1.25447	2.31909	-3.80697	H	-2.84084	2.56202	4.71169
O	-2.62532	0.89203	0.65338	H	-1.48073	3.68118	4.75845
O	-2.64058	-1.27847	0.07136	H	8.85597	-0.89868	-1.84521
O	3.88612	1.88613	2.39378	H	7.26596	-1.33561	-2.54244
O	3.02854	0.25394	3.67441	H	7.70357	-1.92687	-0.94052
O	2.339	-0.21211	-3.89117	H	-2.36915	-6.17398	3.39419
O	3.56452	-1.79459	-2.87475	H	-1.63502	-5.80899	1.80306
N	-8.93581	-0.04549	0.07222	H	-2.93712	-4.79104	2.41049
C	-0.16276	6.52188	1.72988	H	4.84269	-5.32319	4.63165

Continued on next page

Table S4 – Continued from previous page

Atom	X	Y	Z	Atom	X	Y	Z
C	-3.50252	-2.62731	-4.12086	H	3.18811	-4.67303	4.42033
C	-1.74278	4.51343	-4.24362	H	4.51359	-3.57016	4.78149
C	4.30673	6.45062	-0.16272	H	4.31441	-0.54364	-7.17407
C	4.18242	1.14385	6.02463	H	3.76267	0.70804	-6.01543
C	-1.93119	2.82003	5.2775	H	2.62245	-0.50269	-6.58981
C	7.79305	-1.06007	-1.61489	H	-0.02959	-7.62027	-1.78637
C	-2.04949	-5.36465	2.7222	H	-0.8101	-6.08107	-2.26034
C	4.25645	-4.48619	4.2258	H	-0.61035	-6.46082	-0.5528
C	3.67496	-0.35242	-6.30026	H	7.35071	2.16956	-0.32429
C	-0.1254	-6.55356	-1.53783	H	8.91294	1.40023	-1.01969
C	7.8528	1.30769	-0.76791	H	-2.82702	5.47916	-0.30338
C	7.18116	0.16895	-0.99963	H	-2.41837	7.2233	0.25543
C	-2.17803	6.15629	0.25642	H	1.52307	4.12659	-5.4707
C	-1.11619	5.68081	0.92636	H	0.25486	5.4209	-5.95801
C	0.52345	4.55032	-5.3528	H	4.37871	4.67789	-3.19015
C	-0.34622	4.00967	-4.48482	H	4.79541	6.48578	-2.90205
C	4.47602	5.51975	-2.50079	H	5.47993	-4.91359	0.96899
C	4.20632	5.36139	-1.1954	H	5.89608	-5.90465	2.50593
C	5.34154	-5.08643	2.03803	H	3.31761	-5.95326	-1.79894
C	4.50947	-4.31309	2.75284	H	2.39651	-7.56726	-2.05265
C	2.37304	-6.50043	-1.81343	H	0.13703	-3.96781	5.07855
C	1.21725	-5.87452	-1.54201	H	-0.96124	-5.47703	5.26311
C	-0.59728	-4.65054	4.64639	H	0.15295	0.23919	6.4116
C	-1.03894	-4.47329	3.39125	H	-0.88101	1.4287	7.42823
C	-0.54416	1.07875	6.4485	H	-1.63212	-0.18435	-5.80137
C	-0.97364	1.66059	5.3176	H	-3.11744	-1.1439	-6.42525
C	-2.40311	-0.93655	-5.62362	H	5.24687	-2.78815	-4.32791
C	-2.46951	-1.58403	-4.44975	H	5.61283	-2.32192	-6.10735
C	5.02349	-2.16881	-5.19895	H	5.21046	3.49263	3.63381
C	4.04885	-1.24688	-5.15036	H	5.60587	3.45335	5.46846
C	5.11077	3.00182	4.60412	H	1.01269	-2.14738	-2.68051

Continued on next page

Table S4 – Continued from previous page

Atom	X	Y	Z	Atom	X	Y	Z
C	4.38871	1.87699	4.72709	H	1.04164	3.23729	-1.04009
C	-5.40418	1.05556	0.47806	H	-1.26031	-0.75275	2.20759
C	-6.7951	1.09303	0.40679	H	4.25894	-0.58598	1.55246
C	-10.3275	-1.38892	-3.1351	H	-12.4484	-1.49826	-3.5637
C	-9.327	-1.03631	-2.22823	H	-13.1348	-0.51236	-1.37905
C	-11.6902	-1.21009	-2.83171	H	-13.2195	0.60565	1.15954
C	-12.077	-0.66201	-1.60966	H	-12.6805	1.56611	3.39625
C	-9.72028	-0.50028	-0.99505	H	-8.44686	1.0568	2.67271
C	-4.71343	-0.14726	0.2627	H	-10.3186	1.77588	4.1392
C	-11.0914	-0.2987	-0.68058	H	-8.27405	-1.16969	-2.47994
C	-7.52051	-0.07927	0.13472	H	-10.0428	-1.80995	-4.10279
C	-11.135	0.30225	0.63824	H	-4.89627	-2.24766	-0.18012
C	-9.78834	0.44515	1.06919	H	-7.39548	-2.20026	-0.2668
C	-12.1798	0.70988	1.48009	H	-7.32911	2.0346	0.54638
C	-9.4792	0.96697	2.33205	H	-4.83027	1.96114	0.68177
C	-11.8757	1.24361	2.73149				

Table S5: Calculated molecular orbitals of ZrMc-CB

	Orbital	E (eV)
395	LUMO+2	-1.433
394	LUMO+1	-1.579
393	LUMO	-1.808
392	HOMO	-5.631
391	HOMO-1	-5.995
390	HOMO-2	-7.025

Table S6: Calculated excitation energies and oscillator strengths for the first 10 excited states of ZrMc-CB

Excited State 1	Singlet-A	3.4012 eV	364.53 nm	f=0.2423
392 → 393	0.59651			
392 → 394	0.36402			

Continued on next page

Table S6 – Continued from previous page

Excited State 2	Singlet-A	3.7048 eV	334.65 nm	f=0.0380
392 → 393	-0.37654			
392 → 394	0.57672			
392 → 397	0.13415			
Excited State 3	Singlet-A	3.7966 eV	326.57 nm	f=0.0001
391 → 393	0.60127			
391 → 394	0.35839			
Excited State 4	Singlet-A	3.9299 eV	315.49 nm	f=0.0002
392 → 395	0.693			
Excited State 5	Singlet-A	3.9801 eV	311.51 nm	f=0.0001
392 → 396	0.62667			
392 → 397	0.29632			
Excited State 6	Singlet-A	4.0001 eV	309.95 nm	f=0.0508
391 → 412	-0.16857			
392 → 405	0.67999			
Excited State 7	Singlet-A	4.0325 eV	307.47 nm	f=0.0023
392 → 394	-0.14331			
392 → 396	-0.30095			
392 → 397	0.61304			
Excited State 8	Singlet-A	4.0915 eV	303.03 nm	f=0.0017
392 → 398	0.64263			
392 → 400	-0.22778			
392 → 402	-0.11721			
Excited State 9	Singlet-A	4.0929 eV	302.92 nm	f=0.0000
391 → 393	-0.37037			
391 → 394	0.58417			
391 → 397	0.12191			
Excited State 10	Singlet-A	4.1326 eV	300.02 nm	f=0.0018
392 → 398	0.15374			
392 → 399	0.44707			
392 → 400	0.50493			