Supporting Information

Highly efficient intrinsic phosphorescence from a σ-conjugated poly(silylene) polymer

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This Supporting Information contains:

- spectroscopy techniques used during the experiments;
- the results of the additional *ab initio* calculations;
- data needed to reproduce the calculations performed in this study;
- and spectroscopic data regarding white-light applications of PBMSi.

1. Spectroscopy techniques

Time-resolved fluorescence dynamics of the PBMSi toluene solutions and of the solid films was measured by means of Hamamatsu C5680 streak camera with M5676 synchroscan module coupled to a monochromator. Femtosecond Yb:KGW oscillator (Pharos, Light Conversion Ltd.) with a frequency tripler (HIRO, Light Conversion Ltd.) producing 343 nm sub-100 fs pulses at a 76 MHz repetition rate was employed for the sample excitation. The beam was attenuated and focused into about 100 μm spot on the sample. The measurements were performed at excitation density not exceeding 5 mW/mm^2. The temporal resolution of the whole system was ~4 ps.

Gated detection technique with nanosecond time resolution was used to measure delayed photoluminescence emission from PBMSi as delayed fluorescence (DF) and phosphorescence (Ph). The measurements were performed with a set-up made of nitrogen laser with pulse duration of 4 ns at 337 nm for the sample excitation and a triple-grating monochromator coupled to an intensified CCD camera (PI-MAX from Princeton Instruments) with a time-gated, intensified diode array detector synchronized to the laser for luminescence detection. The detection window was selected between 100 ns and 10 ms. A variable time delay (t_{del}) of 75 ns to 10 ms after optical excitation allowed the detection of weak delayed luminescence after the intense prompt fluorescence. To increase the signal-to-noise ratio, spectra were accumulated by averaging over 100-300 pulses. Experimental details were described elsewhere [1]. Prompt fluorescence (PF) component was measured with this set-up during the laser pulse excitation. Measurements of both frozen diluted solutions and films were carried out in a nitrogen-flow cryostat within a temperature range from 77 K to 300 K.

The steady-state continuous wave photoluminescence (cw-PL) spectra were measured at temperatures ranging from 5 K to 300 K using an optical helium cryostat. The luminescence was excited with a 250 W high-pressure mercury lamp using band-pass filters to select different emission lines of the lamp. The PL spectra were monitored with a double-grating spectrometer using a photomultiplier tube. The measurements were taken in a helium atmosphere at ambient pressure. All PL spectra were corrected for the background and instrument spectral response. The absolute PL quantum yield (Φ) of the PBMSi films has been determined at room temperature by comparing the spectrally integrated PL intensity of the above films with the PL signal from a reference sample in the same experimental geometry. As a reference sample we used a cuvette with THF solution of tri-*p*-tolylamine ($c = 10^{-4} - 10^{-3}$ M^{-1}), for which absolute quantum yield of $\Phi = 5\%$ has been established before [2], and a solid polystyrene film doped with tri-*p*-tolylamine.

[1] Kadashchuk, A.; Schols, S.; Vakhnin, A.; Genoe, J.; Heremans, P. Triplet Dynamics and Charge Carrier Trapping in Triplet-Emitter Doped Conjugated Polymers. *Chem. Phys.* **2009**, *358*, 147–155.
[2] Skryshevski, Yu. A.; Vakhnin, A. The Influence of Polymer Matrix Parameters on Intersystem Crossing in Dopant Molecules of Aromatic Amines. *Mol. Cryst. Liq. Cryst.* **2005**, *427*, 207–216.

2. Comparison of the results of TD-DFT and GMC-QDPT calculations

Since the TD-DFT, which was used for the calculations described in the main text, is not a wavefunction-based method, *ab initio* GMC-QDPT computation of the electronic excited states in the MSi15-BP oligomer was carried out to verify the wavefunction character of those states. Results of the GMC-QDPT calculations are presented in parenthesis in Table 1 of the main text, and the relevant molecular orbitals are shown in Fig. S2 of this document. These *ab initio* calculations have also proved the lowest triplet state $T_1^{\pi\text{-}\pi^*}$ to be due to the biphenyl group and that the singlet CT state (S^{CT}) is below the $S^{\sigma\text{-}\sigma^*}$ exciton state of the oligosilane chain of the MSi15-BP. Due to the limited active space, the excited state energies are markedly higher than those obtained from experimental measurements. Relative positions of the GMC-QDPT calculated triplet states with respect to the singlets are also different. Notably, the triplet CT state T_3 (5.69 eV) is substantially upward shifted with respect to the singlet CT state (4.84 eV). However, this discrepancy is the result of an inherently worse accuracy of the estimated triplet states' energies because the singlet reference states were used to initialize the GMC-QDPT calculations of both singlet and triplet excited states. Regardless of that, the arrangement and the wavefunction character of singlet and triplet excited states obtained by the GMC-QDPT calculations qualitatively agree with the results of the TD-DFT calculations. It was also observed that all excited GMC-QDPT states strictly correspond to the single-electron excitations. This validates the assumption that the MSi15-BP oligomer system can be appropriately described by the TD-DFT method.

3. Additional Figures and Tables of quantum-mechanical calculations

The following material contains two Figures and four Tables. Figures S1 and S2 show the shapes of molecular orbitals associated with low-lying electronic excitations from the ground state of the MSi15-BP compound that is used to model the PBMSi polymer during the reported investigation. Tables S1–S4 contain geometric data of the four investigated conformations of the MSi15-BP compound (corresponding to different stages of the photoexcitation life-cycle), as well as *Gaussian09* job information for the excited-state calculations and the total energy values obtained during the calculations.

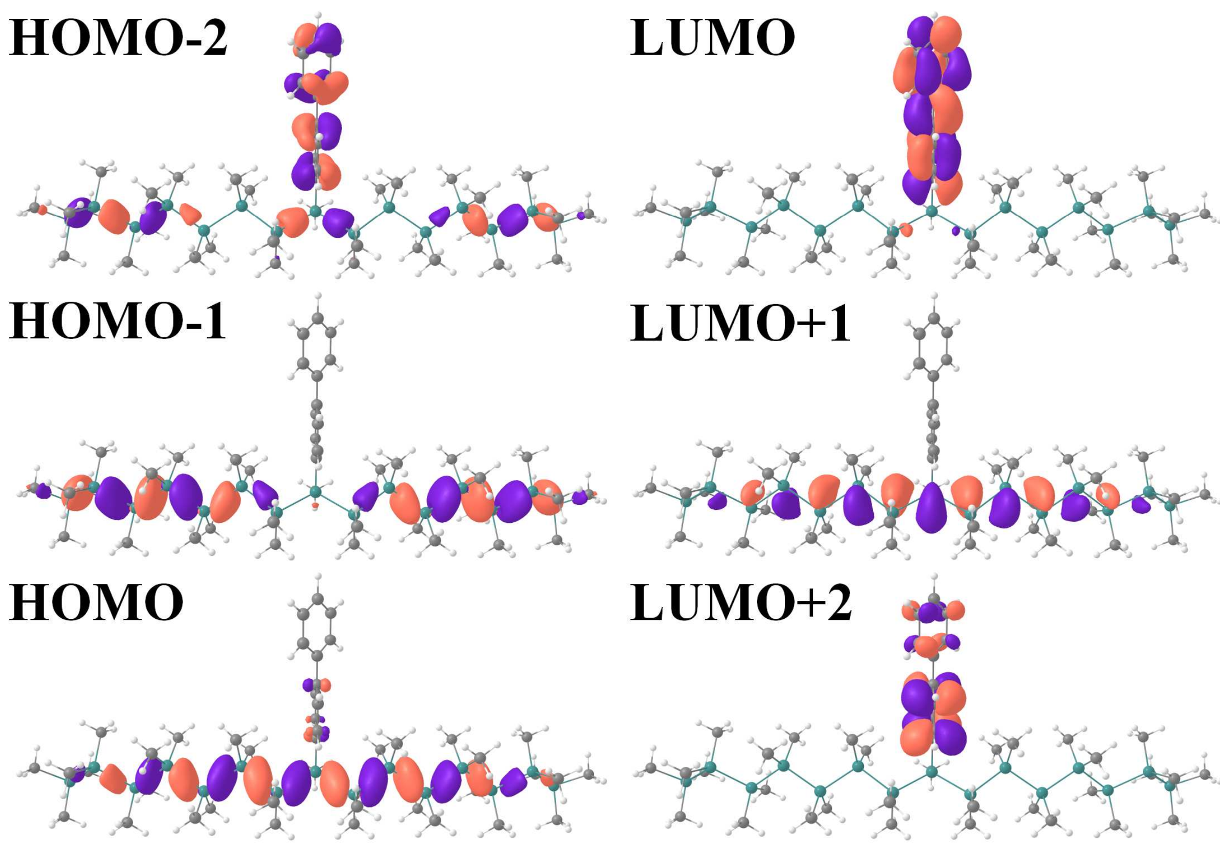

Figure S1. Frontier molecular orbitals of MSi15-BP model compound, based on TD-DFT calculations.

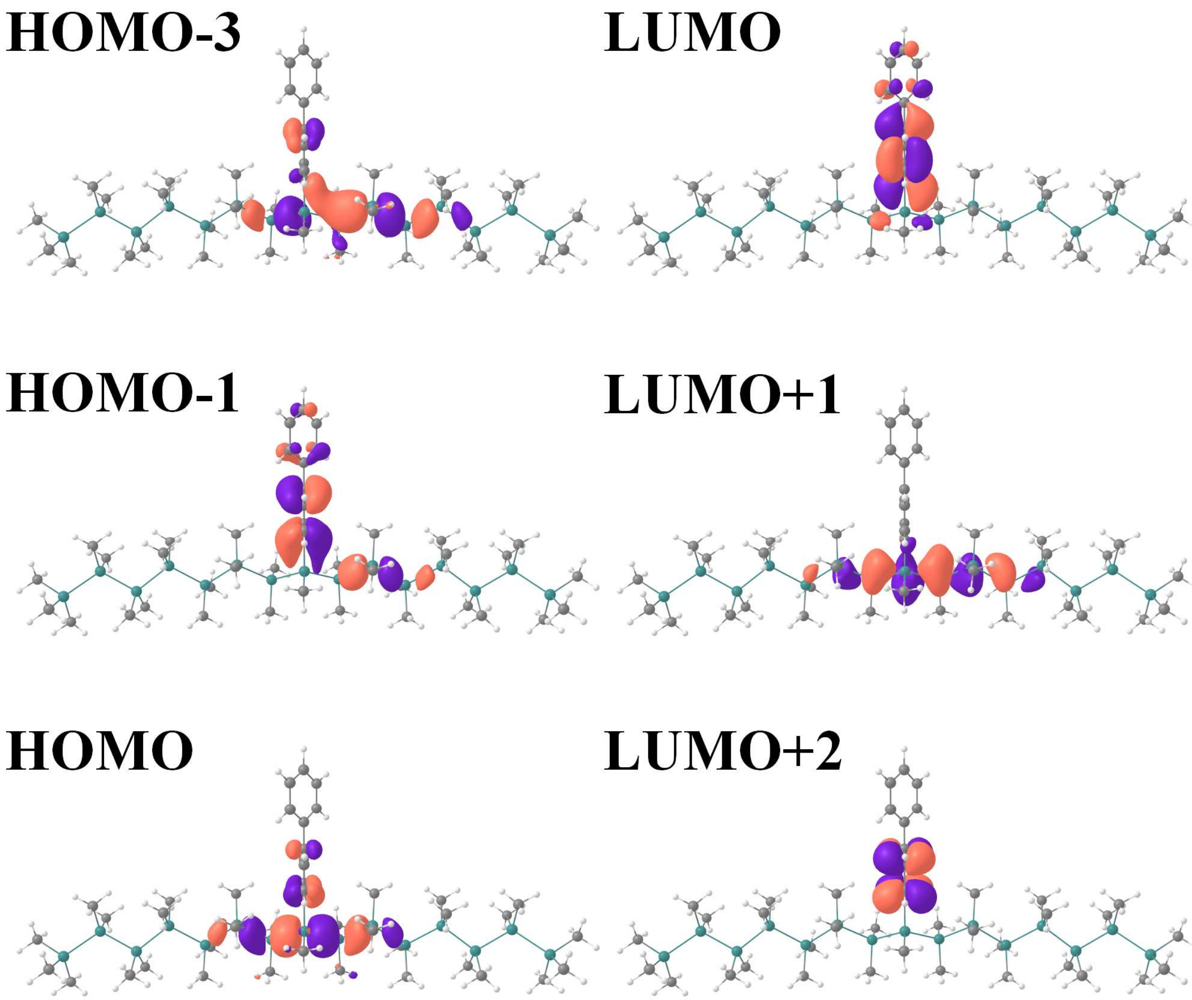

Figure S2. MCSCF optimized frontier molecular orbitals of MSi15-BP model compound, based on GMC-QDPT calculations.

Table S1. Geometric parameters of the ground-state structure (S_0) of MSi15-BP compound.

Charge = 0 Multiplicity = 1			
Si	-0.1496	-0.46347	-1.0007
Si	1.71715	0.03916	0.38247
Si	2.83162	2.04158	-0.26304
Si	5.00514	2.22082	0.70266
Si	5.85903	4.43795	0.47656
Si	8.21789	4.53803	0.79496
Si	8.96742	6.79254	1.03703
Si	11.27981	6.98914	0.47672
Si	12.27602	9.08322	1.04189
Si	14.63388	9.05815	0.66671
Si	15.48592	11.27339	0.43333
Si	17.86169	11.34134	0.62265
Si	18.75781	13.36196	-0.26926
Si	21.02049	13.70237	0.39124
Si	22.12892	15.32574	-0.94291
C	23.83003	15.71519	-0.17827
C	-1.13858	-1.89381	-0.2235
C	0.41132	-1.00491	-2.73671
C	-1.30976	1.03387	-1.18352
C	1.10308	0.23375	2.1848
C	2.90885	-1.45742	0.3325
C	3.01043	2.11283	-2.16709
C	1.74487	3.52045	0.27911
C	4.95174	1.78522	2.56429
C	6.15354	0.95856	-0.16231
C	5.45046	5.13077	-1.26025
C	4.98183	5.54381	1.76858
C	8.7167	3.58484	2.37511
C	9.07173	3.69922	-0.69575
C	8.0036	7.9777	-0.11596

C	8.63189	7.34511	2.83681
C	11.41043	6.77919	-1.41991
C	11.42299	10.43849	-0.00548
C	12.00079	9.51951	2.88408
C	15.45146	8.17546	2.15213
C	15.07916	8.08121	-0.9154
C	14.93444	11.94495	-1.27186
C	14.76006	12.41997	1.78303
C	18.31919	11.17063	2.47239
C	18.65926	9.87201	-0.3086
C	18.63356	13.28574	-2.17741
C	17.7402	14.87296	0.31842
C	22.02018	12.07285	0.29706
C	21.04749	14.29113	2.21186
C	21.13784	16.9477	-1.04005
C	22.41024	14.68346	-2.71212
H	23.73454	16.13247	0.82983
H	24.36963	16.44777	-0.7903
H	24.45556	14.8187	-0.10871
H	-1.99584	-2.15902	-0.85362
H	-1.52426	-1.62679	0.76611
H	-0.5226	-2.79218	-0.10801
H	-0.45449	-1.25818	-3.36002
H	0.9685	-0.2133	-3.24838
H	1.05619	-1.88922	-2.69368
H	-1.64661	1.40596	-0.21016
H	-2.20205	0.76281	-1.76021
H	-0.82	1.86331	-1.70507
H	0.60584	-0.6797	2.52948
H	0.38723	1.05702	2.27874
H	1.93373	0.43716	2.86903
H	3.73957	-1.33014	1.03513

H	2.38698	-2.38153	0.60546
H	3.33565	-1.60148	-0.66541
H	3.53585	3.02077	-2.48111
H	2.02953	2.11397	-2.65505
H	3.57225	1.25497	-2.5509
H	0.7356	3.44253	-0.13952
H	1.6482	3.56846	1.36874
H	2.17058	4.47121	-0.05966
H	4.25533	2.43142	3.10849
H	5.93966	1.90217	3.02277
H	4.63544	0.74788	2.71921
H	7.15341	0.96066	0.28515
H	5.75493	-0.05797	-0.07592
H	6.26549	1.18105	-1.22854
H	5.84809	6.14328	-1.38522
H	4.36806	5.18046	-1.42095
H	5.87594	4.50727	-2.05359
H	3.89399	5.50899	1.64648
H	5.21076	5.2235	2.79024
H	5.29252	6.58962	1.67008
H	8.21518	3.98624	3.26199
H	9.79652	3.64875	2.545
H	8.45391	2.52418	2.29507
H	10.15702	3.66772	-0.55314
H	8.72217	2.66853	-0.8183
H	8.86779	4.23168	-1.63057
H	8.35616	9.00888	-0.00358
H	6.93295	7.96984	0.11555
H	8.11864	7.70147	-1.16907
H	9.21541	6.76044	3.55505
H	8.88427	8.40098	2.98154
H	7.57376	7.22161	3.09288

H	12.44707	6.83153	-1.76692
H	10.99152	5.82349	-1.75094
H	10.85445	7.57494	-1.92648
H	11.82804	11.42931	0.22659
H	10.34607	10.46945	0.19315
H	11.55729	10.26748	-1.07845
H	10.93687	9.62173	3.12203
H	12.41959	8.75475	3.54582
H	12.48658	10.47024	3.12994
H	15.02042	7.17985	2.30062
H	15.31401	8.74085	3.07969
H	16.52848	8.05162	1.99341
H	16.15774	8.11465	-1.10219
H	14.79304	7.02886	-0.81554
H	14.57722	8.48697	-1.79992
H	15.27251	12.97613	-1.42158
H	13.84325	11.93866	-1.3651
H	15.33997	11.3401	-2.0898
H	14.99623	12.0535	2.78754
H	15.16428	13.4345	1.69737
H	13.66981	12.49099	1.70257
H	17.92902	12.00509	3.06404
H	19.40583	11.14496	2.60884
H	17.91053	10.24567	2.89346
H	19.75174	9.90729	-0.23821
H	18.33264	8.91494	0.11271
H	18.39594	9.87535	-1.37137
H	18.95616	14.22956	-2.63083
H	17.60348	13.09957	-2.49916
H	19.25943	12.48775	-2.59004
H	17.72316	14.94876	1.41058
H	18.1651	15.80515	-0.0698

H	16.70259	14.81447	-0.02839
H	23.06612	12.24105	0.57736
H	21.61472	11.31798	0.97952
H	22.01315	11.64803	-0.71196
H	20.50535	15.23407	2.33765
H	22.07551	14.45059	2.55549
H	20.58649	13.55202	2.87566
H	20.94726	17.36394	-0.04504
H	21.68836	17.70279	-1.6137
H	20.1694	16.80244	-1.53091
H	22.95384	15.42547	-3.30899
H	21.46504	14.47396	-3.22341
H	23.00077	13.761	-2.71545
C	12.26906	5.58946	1.30924
C	12.98823	4.63705	0.56403
C	12.32243	5.46458	2.71166
C	13.71915	3.6214	1.1799
H	12.98961	4.68835	-0.52148
C	13.04953	4.45157	3.33262
H	11.77729	6.1679	3.33755
C	13.7662	3.50651	2.57806
H	14.28266	2.92306	0.56769
H	13.04203	4.37458	4.41605
C	14.54344	2.42684	3.23697
C	14.6037	1.13718	2.68183
C	15.24007	2.66499	4.43412
C	15.33354	0.12359	3.30026
H	14.05163	0.9222	1.77183
C	15.96878	1.65131	5.0537
H	15.2309	3.66059	4.86761
C	16.01928	0.37559	4.48963
H	15.35872	-0.86769	2.8567

H	16.50589 1.86134 5.97426
H	16.5875 -0.41426 4.97194
***Gaussian09* job description:** #p b3lyp/6-31(d,p) td=(50-50,nstates=12) fchk	
Total energy: E(RB+HF-LYP) = -6043.01687030	

Table S2. Geometric parameters of the intersection point structure (S^X) of MSi15-BP compound.

Charge = 0 Multiplicity = 1			
Si	13.932066056	-1.384884108	-0.674567052
Si	11.982684917	-0.124495010	-0.157436012
Si	10.012110758	-1.466596113	-0.061160005
Si	8.028027604	-0.130091010	-0.133309010
Si	6.052510453	-1.358640102	0.435717033
Si	4.027433308	-0.175532014	-0.085804006
Si	2.066629159	-1.188652092	0.864327066
Si	-0.016702001	-0.359687028	-0.098870008
Si	-2.079865157	-1.137593087	0.917583068
Si	-4.028227307	-0.163978013	-0.099569007
Si	-6.058227473	-1.321913100	0.461729035
Si	-8.015230616	-0.125132009	-0.230637018
Si	-10.001363750	-1.449822110	-0.070972005
Si	-11.972333892	-0.113241009	-0.240007018
Si	-13.922409047	-1.421450108	-0.621987048
C	-15.474250170	-0.332920025	-0.432321033
C	15.481567157	-0.305966023	-0.419836032
C	13.895506046	-1.955149150	-2.489562190
C	14.085117081	-2.916874221	0.442908034
C	12.219869939	0.721035054	1.542207118
C	11.798459901	1.252686095	-1.471909111
C	9.952623774	-2.684436204	-1.535242118
C	10.080081776	-2.501586192	1.545673118
C	8.167266627	1.339547101	1.079966081

C	7.871807601	0.582512045	-1.901776147
C	6.010836475	-3.023188232	-0.501871038
C	6.114554475	-1.735835132	2.308051176
C	4.095332311	1.610374122	0.584304045
C	3.857251297	-0.087309007	-1.986738153
C	2.068323156	-3.081896235	0.607262046
C	2.091670160	-0.855186064	2.744559212
C	-0.033694003	-0.949180072	-1.914366147
C	-2.103139161	-3.041569230	0.769089058
C	-2.103886158	-0.686170052	2.772583211
C	-4.110193312	1.654727124	0.473447036
C	-3.845640296	-0.180457014	-2.000524152
C	-5.995876475	-3.042390233	-0.364135028
C	-6.160933474	-1.576273120	2.352773178
C	-8.160431615	1.432134112	0.866394064
C	-7.822759590	0.445318034	-2.046917158
C	-9.961160779	-2.756439209	-1.466315110
C	-10.054570776	-2.375522180	1.601423121
C	-11.807945879	1.154354088	-1.662332126
C	-12.188730927	0.858399064	1.392803108
C	-14.044594063	-2.853280218	0.624235046
C	-13.913355036	-2.142658166	-2.382558184
H	-15.552250209	0.085379006	0.576740044
H	-16.381615264	-0.919540071	-0.619465048
H	-15.469760207	0.503654039	-1.139282088
H	16.388704229	-0.869405067	-0.669296050
H	15.573536205	0.027219002	0.619250048
H	15.461793179	0.586620043	-1.054355082
H	14.804362150	-2.516582192	-2.736749207
H	13.038136983	-2.604521200	-2.694697205
H	13.837337031	-1.102862083	-3.175153242
H	14.093721080	-2.643686201	1.503445117

H	15.016472161	-3.456251266	0.233110018
H	13.255871990	-3.615605274	0.287381022
H	13.097039015	1.377642106	1.531751115
H	12.363597919	-0.012882001	2.341955181
H	11.350541893	1.333065103	1.804894138
H	10.963250823	1.919579146	-1.231727094
H	12.704773996	1.866544140	-1.524693118
H	11.619085906	0.839214066	-2.469478188
H	9.031902669	-3.278540253	-1.518768116
H	10.796311806	-3.383169258	-1.501738113
H	9.992253752	-2.159392163	-2.494951188
H	11.000792827	-3.093567234	1.592447121
H	10.049343775	-1.866928143	2.437157185
H	9.237252705	-3.198757247	1.602281123
H	8.334453617	1.002560076	2.108057160
H	7.252246560	1.940801149	1.071506082
H	8.999101670	1.997427152	0.804547061
H	7.023683529	1.272248096	-1.974312150
H	8.773130655	1.138882088	-2.181114164
H	7.725031612	-0.206405016	-2.646293203
H	5.095580390	-3.579803274	-0.272084021
H	6.860687517	-3.654717277	-0.219969017
H	6.048185488	-2.877379219	-1.586017120
H	7.046235529	-2.246773170	2.572702196
H	6.056530454	-0.821210064	2.906642224
H	5.284290405	-2.385653183	2.606810199
H	4.325456330	1.633553123	1.654045126
H	3.132154241	2.111654163	0.439120033
H	4.859119373	2.199679168	0.064324005
H	3.001650231	0.537150040	-2.266905173
H	4.750074362	0.357398027	-2.439221188
H	3.714211284	-1.076472082	-2.433411186

H	1.168601090	-3.538219271	1.034040079
H	2.933250224	-3.537766269	1.102986085
H	2.109986159	-3.350049255	-0.452822035
H	2.040476155	0.214936016	2.965526226
H	1.250183098	-1.345067103	3.247414248
H	3.015116231	-1.242394095	3.189286244
H	-0.920757068	-0.594443045	-2.449510187
H	0.851055063	-0.599994045	-2.457147189
H	-0.037633003	-2.042625155	-1.961191147
H	-2.985891227	-3.459230264	1.266814096
H	-1.220143092	-3.483804266	1.243202096
H	-2.121604161	-3.368203257	-0.275130021
H	-1.263689098	-1.146965085	3.304287250
H	-2.045103154	0.395859030	2.923450222
H	-3.028415233	-1.038817078	3.242881247
H	-3.153069242	2.157747163	0.299031023
H	-4.341267332	1.732806132	1.540251120
H	-4.880070373	2.206545169	-0.077870006
H	-4.738934361	0.229860018	-2.483377187
H	-2.992807229	0.434682033	-2.307646175
H	-3.691155280	-1.191872093	-2.389704183
H	-6.850512550	-3.656292278	-0.058940004
H	-5.084921390	-3.580349273	-0.079771006
H	-6.010453457	-2.965634226	-1.455766109
H	-6.125606448	-0.624101048	2.891464219
H	-7.094243547	-2.079167156	2.628468201
H	-5.332411398	-2.196539168	2.712565208
H	-8.332818618	1.174543089	1.916260147
H	-8.990018660	2.068267158	0.538049043
H	-7.245025566	2.030906154	0.817513062
H	-8.709620654	0.991965074	-2.385060182
H	-6.960916545	1.112524087	-2.162549166

H	-7.679835589	-0.403923031	-2.722796210
H	-10.811043836	-3.443489262	-1.384358106
H	-9.045856703	-3.356501254	-1.420248108
H	-10.004152779	-2.291136173	-2.456157188
H	-10.015558771	-1.681613128	2.447232185
H	-10.974076837	-2.962925225	1.697826129
H	-9.210412729	-3.066685236	1.697777127
H	-12.713906961	1.764476136	-1.750820135
H	-10.968056864	1.836575139	-1.491193113
H	-11.645193871	0.660342048	-2.625450203
H	-12.320531940	0.186461014	2.247203169
H	-13.067533997	1.510930118	1.344215101
H	-11.317587856	1.489047114	1.597982125
H	-14.042768084	-2.487761188	1.656612127
H	-14.972789162	-3.417563260	0.474719036
H	-13.210405027	-3.555502269	0.519050039
H	-14.823229119	-2.727426209	-2.563145196
H	-13.056102022	-2.803464212	-2.547457197
H	-13.873527040	-1.352458105	-3.140080242
C	-0.008041001	1.526911117	-0.057140004
C	-0.063840005	2.312692177	-1.228633095
C	0.058301004	2.233721172	1.164924091
C	-0.062333005	3.701666285	-1.185610090
H	-0.120492009	1.825562140	-2.198307170
C	0.062410005	3.621890275	1.213416095
H	0.116455009	1.677761130	2.097390158
C	-0.000511000	4.397714335	0.038297003
H	-0.143615011	4.261048326	-2.112566163
H	0.149802011	4.118726316	2.174703166
C	0.000328000	5.875175431	0.085398006
C	0.585149046	6.638149486	-0.944393071
C	-0.586717046	6.572220510	1.159805090

C	0.582400045	8.029315621	-0.902102067
H	1.076141082	6.133364451	-1.770225133
C	-0.588561044	7.963445595	1.202105090
H	-1.076515083	6.016269485	1.952967151
C	-0.004352000	8.702274668	0.171410013
H	1.049425082	8.591173640	-1.706060132
H	-1.057454082	8.474012633	2.038501155
H	-0.006484000	9.787443741	0.204157016

***Gaussian09* job description:** #p b3lyp/6-31(d,p) td=(50-50,nstates=12) fchk

Total energy (of S_0): E(RB+HF-LYP) = -6042.99826887

Table S3. Geometric parameters of the optimized S^{CT} state structure (S^{CT}_{min}) of MSi15-BP compound.

Charge = 0 Multiplicity = 1

Si	13.511327000	-0.844501000	-0.528953000
Si	11.499471000	0.055234000	0.366048000
Si	9.601414000	-1.251583000	-0.246318000
Si	7.583745000	-0.036538000	0.142007000
Si	5.716537000	-1.529786000	0.161566000
Si	3.709745000	-0.236987000	-0.094076000
Si	1.899338000	-1.684063000	0.590149000
Si	-0.008911000	-0.618616000	-0.431173000
Si	-1.922369000	-1.666482000	0.595893000
Si	-3.729083000	-0.219025000	-0.092782000
Si	-5.739521000	-1.505425000	0.160325000
Si	-7.606589000	-0.012948000	0.136282000
Si	-9.624545000	-1.226675000	-0.253313000
Si	-11.524084000	0.078662000	0.356890000
Si	-13.534861000	-0.822853000	-0.538550000
C	-15.024604000	0.033072000	0.281402000
C	14.999510000	0.012886000	0.292205000
C	13.602430000	-0.534544000	-2.403022000

C	13.648570000	-2.714295000	-0.205538000
C	11.627460000	0.097880000	2.273584000
C	11.313668000	1.852882000	-0.256833000
C	9.662813000	-1.703552000	-2.102173000
C	9.632770000	-2.876380000	0.760339000
C	7.636862000	0.866815000	1.822642000
C	7.396022000	1.271762000	-1.235519000
C	5.818149000	-2.790711000	-1.267451000
C	5.732807000	-2.486806000	1.812690000
C	3.715169000	1.284867000	1.038006000
C	3.565411000	0.313635000	-1.906596000
C	2.109760000	-3.479937000	-0.019819000
C	1.893820000	-1.704824000	2.494513000
C	-0.012168000	-1.197167000	-2.247127000
C	-2.134770000	-3.463708000	-0.009215000
C	-1.914683000	-1.682817000	2.500340000
C	-3.732813000	1.305124000	1.037023000
C	-3.577611000	0.330522000	-1.905422000
C	-5.840614000	-2.768650000	-1.267000000
C	-5.758578000	-2.460630000	1.812808000
C	-7.661737000	0.893199000	1.815573000
C	-7.416015000	1.293806000	-1.242626000
C	-9.684493000	-1.679044000	-2.109226000
C	-9.656962000	-2.851654000	0.753211000
C	-11.339342000	1.876128000	-0.267009000
C	-11.653331000	0.122701000	2.264385000
C	-13.670782000	-2.692743000	-0.214876000
C	-13.625421000	-0.513504000	-2.412796000
H	-15.043158000	-0.135831000	1.363166000
H	-15.964031000	-0.354125000	-0.130868000
H	-15.012199000	1.115356000	0.113922000
H	15.939619000	-0.372773000	-0.119947000

H	15.017835000	-0.156739000	1.373852000
H	14.985710000	1.095258000	0.125436000
H	14.545310000	-0.916674000	-2.811452000
H	12.784528000	-1.027156000	-2.938796000
H	13.551979000	0.535214000	-2.632298000
H	13.575378000	-2.945031000	0.862681000
H	14.613607000	-3.094968000	-0.560191000
H	12.863632000	-3.276552000	-0.722581000
H	12.492396000	0.691451000	2.589659000
H	11.744316000	-0.907088000	2.692168000
H	10.736340000	0.545871000	2.725905000
H	10.451174000	2.348863000	0.201076000
H	12.201677000	2.444256000	-0.007430000
H	11.184917000	1.891767000	-1.343244000
H	8.789704000	-2.296336000	-2.394734000
H	10.555383000	-2.295497000	-2.332270000
H	9.684343000	-0.809754000	-2.733919000
H	10.578148000	-3.408308000	0.608137000
H	9.529939000	-2.689245000	1.834065000
H	8.824362000	-3.551250000	0.458334000
H	7.783236000	0.169857000	2.653878000
H	6.709226000	1.418695000	2.006648000
H	8.459095000	1.590356000	1.845490000
H	6.526036000	1.913348000	-1.060039000
H	8.277091000	1.921197000	-1.276142000
H	7.280388000	0.810239000	-2.221374000
H	4.950530000	-3.458467000	-1.269337000
H	6.713003000	-3.416047000	-1.173101000
H	5.858171000	-2.293989000	-2.241902000
H	6.671982000	-3.037488000	1.932083000
H	5.632712000	-1.813016000	2.669375000
H	4.917008000	-3.215571000	1.860564000

H	3.909924000	1.018327000	2.081669000
H	2.751707000	1.802920000	0.990701000
H	4.488309000	1.993896000	0.720907000
H	2.700736000	0.973685000	-2.026826000
H	4.455687000	0.876216000	-2.206955000
H	3.459813000	-0.532956000	-2.592096000
H	1.237803000	-4.086617000	0.250346000
H	2.987053000	-3.954443000	0.433159000
H	2.222592000	-3.527641000	-1.106967000
H	1.700383000	-0.710692000	2.907111000
H	1.124320000	-2.383754000	2.876273000
H	2.857013000	-2.050738000	2.884661000
H	-0.891690000	-0.813294000	-2.773651000
H	0.870768000	-0.822234000	-2.774352000
H	-0.017442000	-2.288263000	-2.329325000
H	-3.012795000	-3.935371000	0.445219000
H	-1.263730000	-4.070786000	0.262811000
H	-2.247973000	-3.514501000	-1.096177000
H	-1.146552000	-2.362415000	2.883530000
H	-1.719244000	-0.688162000	2.910748000
H	-2.878611000	-2.025744000	2.891385000
H	-2.768100000	1.821049000	0.990453000
H	-3.929831000	1.040714000	2.080829000
H	-4.504258000	2.014961000	0.717549000
H	-4.462786000	0.900353000	-2.207242000
H	-2.707055000	0.982874000	-2.025039000
H	-3.478061000	-0.517161000	-2.590496000
H	-6.736948000	-3.392019000	-1.173774000
H	-4.974342000	-3.438193000	-1.266122000
H	-5.877550000	-2.273328000	-2.242313000
H	-5.659611000	-1.785708000	2.668762000
H	-6.698006000	-3.010994000	1.931653000

H	-4.942950000	-3.189457000	1.862964000
H	-7.809870000	0.197578000	2.647630000
H	-8.483352000	1.617498000	1.836303000
H	-6.733778000	1.444394000	2.000125000
H	-8.296203000	1.944329000	-1.285224000
H	-6.545347000	1.934464000	-1.066982000
H	-7.299681000	0.830920000	-2.227774000
H	-10.576638000	-2.271369000	-2.340006000
H	-8.810883000	-2.271540000	-2.400934000
H	-9.705766000	-0.785392000	-2.741194000
H	-9.555464000	-2.664604000	1.827086000
H	-10.602061000	-3.383740000	0.599809000
H	-8.848022000	-3.526346000	0.452217000
H	-12.227743000	2.467191000	-0.018245000
H	-10.477190000	2.372826000	0.190786000
H	-11.210255000	1.914371000	-1.353401000
H	-11.769498000	-0.882063000	2.683664000
H	-12.518912000	0.715755000	2.579668000
H	-10.762746000	0.571751000	2.716737000
H	-13.597647000	-2.923215000	0.853411000
H	-14.635431000	-3.074274000	-0.569673000
H	-12.885234000	-3.254465000	-0.731578000
H	-14.567615000	-0.896846000	-2.821682000
H	-12.806617000	-1.005264000	-2.947985000
H	-13.576081000	0.556262000	-2.642319000
C	-0.000683000	1.213536000	-0.298566000
C	0.033209000	2.062316000	-1.448837000
C	-0.010736000	1.895496000	0.960416000
C	0.059410000	3.437025000	-1.355799000
H	0.029487000	1.619402000	-2.443513000
C	0.009149000	3.270987000	1.059232000
H	-0.026151000	1.316653000	1.884362000

C	0.049492000	4.128197000	-0.093433000
H	0.053866000	4.011296000	-2.276207000
H	0.026727000	3.712227000	2.050574000
C	0.079913000	5.567639000	0.006437000
C	0.361067000	6.404177000	-1.119676000
C	-0.169301000	6.256731000	1.234910000
C	0.389497000	7.785922000	-1.020111000
H	0.591516000	5.951958000	-2.078737000
C	-0.139873000	7.639142000	1.321582000
H	-0.420778000	5.690752000	2.126016000
C	0.139822000	8.434252000	0.199105000
H	0.617899000	8.373872000	-1.906834000
H	-0.346471000	8.112160000	2.279517000
H	0.161810000	9.516888000	0.271847000

***Gaussian09* job description:** #p b3lyp/6-31(d,p) td=(50-50,nstates=12) fchk

Total energy (of S_0): E(RB+HF-LYP) = -6043.01462818

Table S4. Geometric parameters of the optimized T_1 state structure (T_1^{min}) of MSi15-BP compound.

Charge = 0 Multiplicity = 1			
Si	13.704951065	-1.211154090	-0.785990058
Si	11.785024884	-0.227325017	0.210668016
Si	9.780703770	-1.397049104	-0.324396025
Si	7.832112586	-0.132405010	0.207258016
Si	5.871947450	-1.494155114	0.224793017
Si	3.897369298	-0.158130012	0.126281010
Si	1.960368150	-1.411997108	0.733650057
Si	-0.009865001	-0.435085033	-0.227636017
Si	-2.030466154	-1.163088090	0.836677063
Si	-3.942663299	-0.135454011	-0.154835012
Si	-5.943914445	-1.308092102	0.399584030
Si	-7.892940612	-0.038412003	-0.125616010

Si	-9.861073728	-1.387551108	-0.108743008
Si	-11.829799894	-0.044979003	-0.041445003
Si	-13.787439056	-1.277148097	-0.586737044
C	-15.328874173	-0.248276019	-0.146498011
C	15.274992181	-0.435929033	-0.035958003
C	13.729120072	-0.896981070	-2.662726205
C	13.771063031	-3.088919238	-0.481574037
C	12.019394895	-0.228095017	2.109975163
C	11.681648892	1.594616123	-0.365647028
C	9.741502742	-1.804228137	-2.193686167
C	9.783553760	-3.052104234	0.635451048
C	8.014651591	0.674230051	1.932744145
C	7.657108590	1.269167099	-1.082955080
C	5.866284460	-2.691487205	-1.266281098
C	5.887242472	-2.540295196	1.826718138
C	4.038912306	1.322443103	1.324966104
C	3.706274281	0.525281040	-1.648031127
C	2.061834157	-3.206892246	0.076696006
C	1.869621142	-1.508051113	2.640568204
C	-0.036593003	-0.998776077	-2.054645157
C	-2.107636162	-3.071365232	0.718697054
C	-2.026078153	-0.703056056	2.691644207
C	-4.023891308	1.665124129	0.479040037
C	-3.783445290	-0.074359006	-2.059472158
C	-5.955888456	-2.963815227	-0.558764041
C	-5.979988458	-1.708476128	2.270168176
C	-8.057888600	1.376053103	1.151524090
C	-7.725409603	0.753266060	-1.859698142
C	-9.861677731	-2.480775191	-1.678454130
C	-9.875723736	-2.543169194	1.415104108
C	-11.692237887	1.424692107	-1.258474099
C	-12.034931909	0.670966049	1.721605132

C	-13.874466065	-2.915932222	0.377283029
C	-13.843987043	-1.666336130	-2.448331186
H	-15.373420155	-0.028825002	0.925520070
H	-16.244720232	-0.789427059	-0.412587032
H	-15.343167197	0.707554052	-0.681325053
H	16.174202231	-0.866389064	-0.492578038
H	15.335317170	-0.611149049	1.043434081
H	15.307908170	0.646715051	-0.198911015
H	14.634032112	-1.320143103	-3.114572237
H	12.865701984	-1.348826103	-3.161971241
H	13.717448062	0.175095013	-2.886871220
H	13.754191061	-3.323958255	0.588131045
H	14.690584121	-3.515720269	-0.899299068
H	12.925835993	-3.605745278	-0.948577075
H	12.931582964	0.309904023	2.390784181
H	12.099770939	-1.246700095	2.503516192
H	11.178270833	0.257400020	2.615982201
H	10.868080835	2.126201161	0.139879011
H	12.611596943	2.130309164	-0.143915011
H	11.507531902	1.665419129	-1.444263108
H	8.816378671	-2.324299177	-2.463800190
H	10.579207790	-2.451550187	-2.476127189
H	9.801229761	-0.897043069	-2.803921215
H	10.684542797	-3.634982279	0.415443032
H	9.752140740	-2.888270222	1.717581131
H	8.918645667	-3.668124279	0.366120028
H	8.165261627	-0.078929006	2.713196205
H	7.121452518	1.250771093	2.196376165
H	8.869752653	1.358490101	1.961101150
H	6.804547526	1.916852148	-0.851709062
H	8.552673667	1.899329147	-1.106185083
H	7.507706559	0.870346066	-2.091731158

H	4.955707376	-3.299783253	-1.278430098
H	6.720625518	-3.376196257	-1.230053094
H	5.914890448	-2.148732163	-2.215932170
H	6.788741531	-3.159427243	1.885337145
H	5.863578459	-1.905630145	2.718783205
H	5.021997383	-3.210405247	1.871851142
H	4.188055320	0.990332075	2.357681181
H	3.134578238	1.939085149	1.296798099
H	4.885841374	1.962849150	1.055726080
H	2.828799213	1.176937092	-1.717278129
H	4.582157351	1.114111084	-1.940275147
H	3.589750276	-0.279869021	-2.381278184
H	1.152885087	-3.771469289	0.310776024
H	2.905130222	-3.739694285	0.530065039
H	2.197874165	-3.232551247	-1.009049075
H	1.755114133	-0.518201040	3.093351235
H	1.029061076	-2.128395161	2.969656227
H	2.785988213	-1.952464147	3.045162232
H	-0.887092065	-0.582925047	-2.602739201
H	0.879778068	-0.699932053	-2.574518194
H	-0.109837008	-2.089492161	-2.116274160
H	-3.006123229	-3.459690262	1.210940091
H	-1.242198093	-3.529802268	1.209840090
H	-2.122093163	-3.416684260	-0.320146025
H	-1.180439092	-1.157232087	3.217832245
H	-1.971267148	0.379964029	2.837597219
H	-2.945228225	-1.054759083	3.173180242
H	-3.082608238	2.190397166	0.286451022
H	-4.213476323	1.705052129	1.556478118
H	-4.824485367	2.221179168	-0.021339002
H	-4.682823358	0.355644027	-2.512674191
H	-2.934337223	0.550130043	-2.356795179

H	-3.638923279	-1.070289080	-2.490763189
H	-6.827875511	-3.570895273	-0.291993022
H	-5.062013386	-3.556189273	-0.336618025
H	-5.982688479	-2.799140215	-1.640926123
H	-5.926123453	-0.798165062	2.876330221
H	-6.902832516	-2.231753172	2.541821195
H	-5.139656394	-2.350124180	2.556827196
H	-8.201171648	0.988350074	2.165467165
H	-8.913068668	2.019608156	0.917882069
H	-7.162972559	2.007316152	1.161891091
H	-8.623419638	1.322597099	-2.122504164
H	-6.874552543	1.442192110	-1.899746144
H	-7.576422554	-0.005904000	-2.634651203
H	-10.718451840	-3.163584242	-1.685341128
H	-8.953106695	-3.089444234	-1.735518133
H	-9.911687733	-1.874808142	-2.589059197
H	-9.814755743	-1.976114152	2.349709178
H	-10.794943830	-3.137836240	1.448560112
H	-9.031427680	-3.240661248	1.392993109
H	-12.600477976	2.037507154	-1.236802094
H	-10.850116855	2.076488160	-1.002425077
H	-11.547714871	1.082549085	-2.288451176
H	-12.149072902	-0.123783010	2.466241190
H	-12.922023006	1.311277098	1.781108134
H	-11.169397853	1.275686097	2.011981151
H	-13.825236070	-2.750928209	1.458972114
H	-14.814760113	-3.438549260	0.165449013
H	-13.054685996	-3.590139275	0.106742008
H	-14.756753132	-2.218963170	-2.700494204
H	-12.989715995	-2.275585173	-2.761001209
H	-13.835329068	-0.750823055	-3.049571231
C	0.066861005	1.443209109	-0.168256013

C	0.019088001	2.261268171	-1.350627104
C	0.168688013	2.160110167	1.080916081
C	0.068572005	3.628256277	-1.309303097
H	-0.057554004	1.779082137	-2.321699176
C	0.218525017	3.524095271	1.152240088
H	0.210161016	1.593686121	2.008732151
C	0.172821013	4.366392334	-0.045605003
H	0.027205002	4.175108321	-2.243143173
H	0.297031023	3.988705302	2.127667161
C	0.227018017	5.770025425	0.009544001
C	0.194882015	6.599424507	-1.190899090
C	0.320322024	6.499251518	1.269879096
C	0.250565019	7.970897628	-1.124407085
H	0.128347010	6.129359479	-2.163953163
C	0.373502028	7.871497609	1.309591102
H	0.346936027	5.951227463	2.203258168
C	0.340543026	8.641173640	0.120152009
H	0.225294017	8.550626650	-2.043083158
H	0.441987034	8.375000659	2.270036172
H	0.383476030	9.724274742	0.162173012

***Gaussian09* job description:** #p b3lyp/6-31(d,p) td=(50-50,nstates=12) fchk

Total energy (of S_0): E(RB+HF-LYP) = -6043.00007062

4. Spectra of PBMSi films doped with organometallic complexes

Since the T_1 level of PBMSi was found to be located at relatively high energy (2.7 eV), triplet excitations of green- and red-colored triplet emitters imbedded into polymer matrix could be perfectly confined in the polymer host and therefore PBMSi polymers could be promising materials for creation of white-light emitting diodes. Moreover, PBMSi polymers exhibit blue fluorescence with high quantum yield. Therefore, we have studied luminescent properties of PBMSi polymers doped with organometallic Ir complexes, namely $Ir(ppy)_3$ and $Btp_2Ir(acac)$ (molecular structures are shown in the inset in Fig. S3), which are efficient triplet emitters in green- and red-light spectral ranges, respectively. Figure S3a compares cw-PL spectra measured in neat PBMSi film (curve 1), PBMSi doped ($C = 1$ wt.%) with $Ir(ppy)_3$ (curve 2) or with $Btp_2Ir(acac)$ (curve 3). The host luminescent emission is slightly quenched upon 1 wt.% doping of the film with these triplet emitters due to energy transfer from the polymer host to guest molecules and new characteristic Ph spectra with the main peaks either at 507 nm or at 614 nm appear due to phosphorescence of $Ir(ppy)_3$ and $Btp_2Ir(acac)$ guest molecules, respectively (curves 2 and 3 in Fig. S3a). The observed Ph spectra of $Ir(ppy)_3$ and $Btp_2Ir(acac)$ are consistent with those earlier reported for these compounds. As the lowest S_0–S_1 transition in $Ir(ppy)_3$ and $Btp_2Ir(acac)$ molecules is at 377 and 485 nm, respectively, the host polymer fluorescence is partially quenched by guest molecules. The host phosphorescence is also quenched (Fig. S3a), which proves the triplet energy transfer of host triplets to the triplet emitter guest molecules.

Figure S3b shows the room-temperature steady-state luminescence spectra of PBMSi film doubly-doped with both $Ir(ppy)_3$ and $Btp_2Ir(acac)$ triplet emitters at identical concentrations equal to $C = 0.2$ wt.% (curve 1) and 0.5 wt.% (curve 2), respectively. Contribution of different emission components to the PL spectrum of the doubly-doped film is very sensitive to the concentration of guest molecules – the host fluorescence dominates the PL spectra of the film at relatively small guest concentration (ca. 0.25 wt.%) (curve 1, Fig. S3b) while the guest phosphorescent components are considerably enhanced at guest concentrations of 0.5 wt.% (curve 2). As a result, the emission of PBMSi film doubly-doped with $Ir(ppy)_3$ and $Btp_2Ir(acac)$ is visually perceived as a white light. The latter result suggests that this polymer can be used as an active polymer host layer for creation of white-light emitting OLED devices.

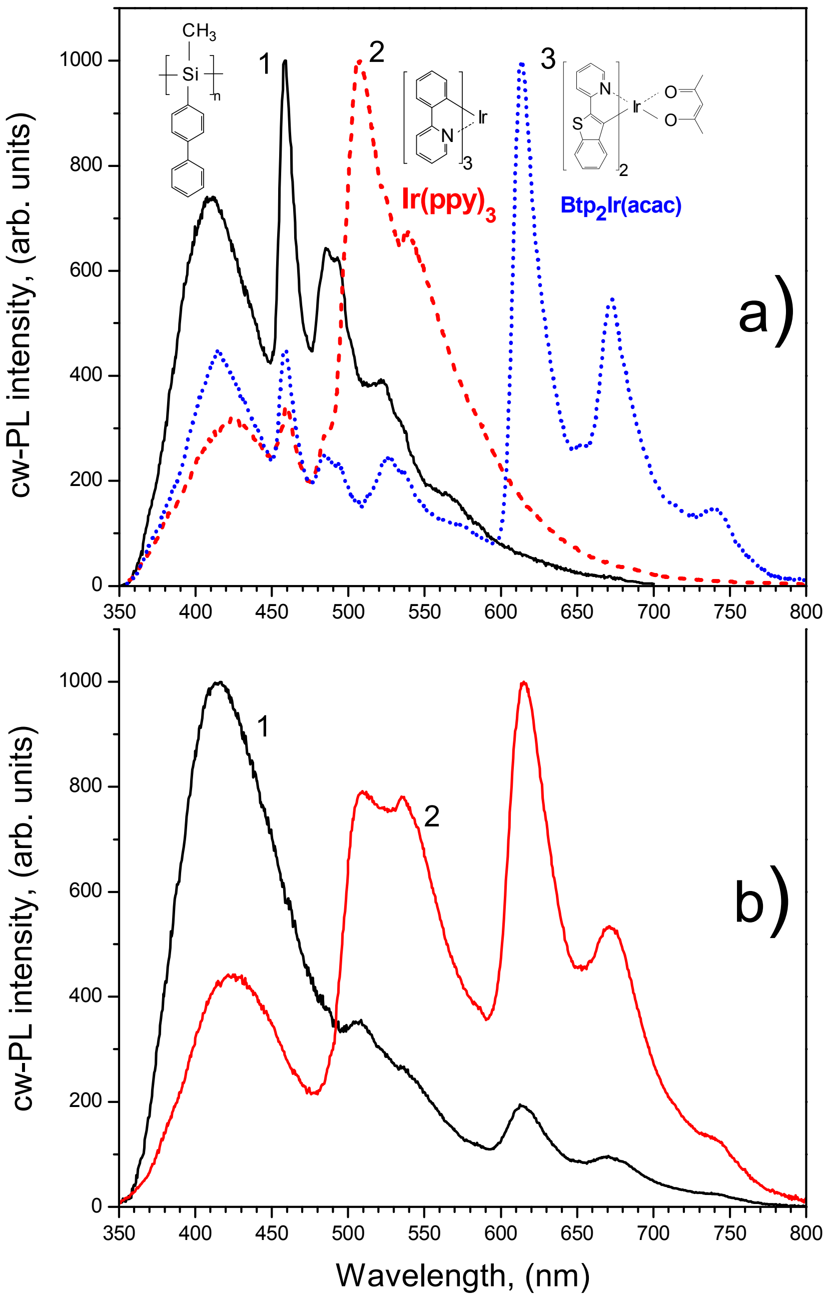

Figure S3. a) Normalized cw-PL spectra measured at 5 K in neat PBMSi(1):PMPSi(1) film (curve *1*) and PBMSi(1):PMPSi(1) film doped ($C = 1$ wt.%) with $Ir(ppy)_3$ (curve *2*) and with $Btp_2Ir(acac)$ (curve *3*). b) Normalized cw-PL spectra measured at room temperature from PBMSi film doubly-doped with $Ir(ppy)_3$ and $Btp_2Ir(acac)$ with the same concentrations of dopants equal to 0.2 wt.% (curve *1*) and 0.5 wt.% (curve *2*). All spectra were measured under the excitation with $\lambda_{exc} = 313$ nm.