applied sciences

MDPI

Electronic Support Materials

Photoluminescence of Metal-Polymer Complexes Based on Functional Triazole-Carbazole Copolymers with Terbium Ions

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1. Deconvolution

The luminescence spectra of metal-polymer complexes in PMMA film were deconvolved to consider the contributions of luminescence bands of different luminescent systems: individual VK units, their excimers, and Tb^{3+} in MPC. In deconvolving the emission spectra (Figure 1, see in the main paper), an asymmetric double sigmoidal *Asym2Sig* function according Equation 1 (see in the main paper) was used with OriginPro [1] to determine the main parameters corresponding to peaks.

Figure S1 shows the deconvolution of the luminescence spectra for the three systems studied in this work. They are metal-polymer complexes based on Tb^{III} ions and poly(VT-*co*-VK) copolymers with 9 (P1), 16 (P2), and 37 mol % (P3) of VK units in a photoinert PMMA matrix (see Table 1 in the main paper).

The main parameters defined for the peaks into which the obtained spectra are decomposed are as follows. The integral area under the curve of the corresponding peak determines the contribution of the luminescence band of the photoprocess associated with the peak to the total photoluminescence spectrum (Area Intg). Integral area under the peak curve expressed as a percentage gives the fraction in the luminescence spectrum (Area IntgP). The center of gravity means a weighted average of the emission wavelengths for all photons emitted in the photoprocess for which the peak in question is responsible (Center Grvty). It is a maximum peak intensity (Max Height), as well as calculated full width of peak at half maximum height (FWHM). These parameters are shown in Figure S1 under the curves presenting the decomposition of the spectra into eight peaks.

P1

Peak Analysis

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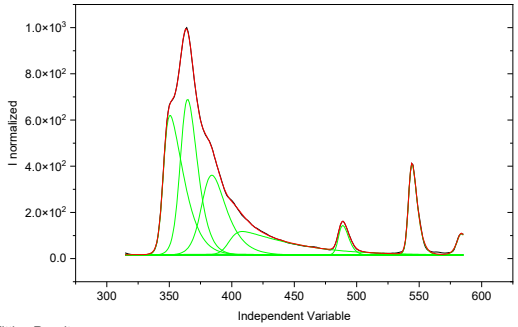

Fitting Results

Peak Index	Peak Type	Area Intg	Area IntgP	Center Grvty	Max Height	FWHM
1	Asym2Sig	12669.76945	27.30468	357.00329	605.27722	18.4362
2	Asym2Sig	12327.94268	26.568	367.26953	674.21926	16.1725
3	Asym2Sig	9327.87351	20.10254	388.56443	346.13076	23.89913
4	Asym2Sig	6198.61845	13.35867	439.67037	102.0076	50.45888
5	Asym2Sig	337.76321	0.72791	347.79812	3.82066	97.31172
6	Asym2Sig	1364.05927	2.93969	490.41425	128.18042	9.59833
7	Asym2Sig	3616.29072	7.79348	546.00964	393.83355	8.10647
8	Asym2Sig	559.1476	1.20502	583.69129	93.56352	8.36839

P2

Peak Analysis

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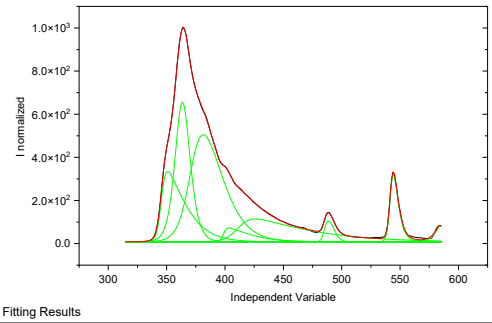
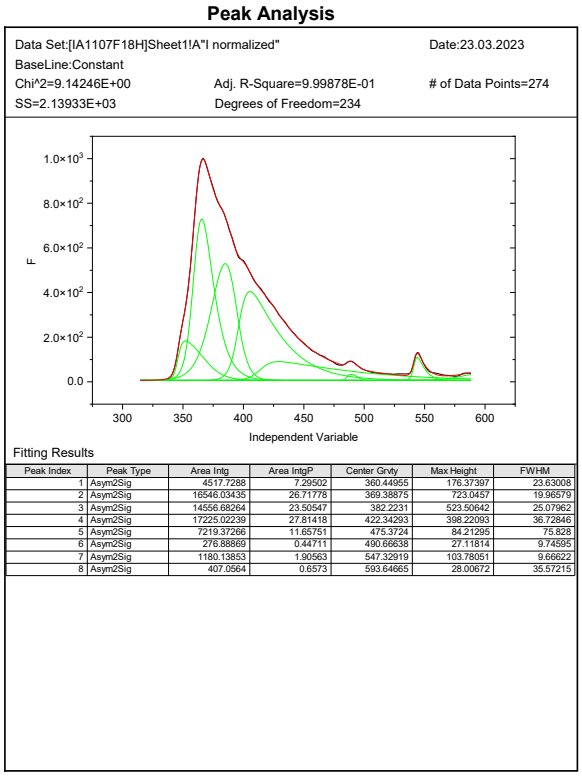


Fitting Results

Peak Index	Peak Type	Area Intg	Area IntgP	Center Grvty	Max Height	FWHM
1	Asym2Sig	8583.23288	16.33538	361.85944	325.90284	22.50332
2	Asym2Sig	11224.27444	21.36174	363.9113	647.92171	15.33983
3	Asym2Sig	18620.29934	35.43765	387.80711	496.56205	33.3321
4	Asym2Sig	1835.0597	3.49244	418.10471	63.82024	24.3977
5	Asym2Sig	7814.18525	14.87175	459.66705	105.61331	63.67497
6	Asym2Sig	997.83441	1.89905	490.17541	96.45652	9.60648
7	Asym2Sig	2977.13457	5.666	546.12701	312.44341	8.30175
8	Asym2Sig	491.80997	0.936	581.77982	72.92286	7.73058



Peak Index	Peak Type	Area Intg	Area IntgP	Center Grvty	Max Height	FWHM
1	Asym2Sig	4517.7288	7.29502	360.44955	176.37397	23.63008
2	Asym2Sig	16546.03435	26.71778	369.38875	723.0457	19.96579
3	Asym2Sig	14556.68264	23.50547	382.2231	523.50642	25.07962
4	Asym2Sig	17225.02239	27.81418	422.34293	398.22093	36.72846
5	Asym2Sig	7219.37266	11.65751	475.3724	84.21295	75.828
6	Asym2Sig	276.88869	0.44711	490.66638	27.11814	9.74595
7	Asym2Sig	1180.13853	1.90563	547.32919	103.78051	9.66622
8	Asym2Sig	407.0564	0.6573	593.64665	28.00672	35.57215

Figure S1. Deconvolution of photoluminescence spectra for MPC based on Tb^{3+} ions and poly(VT-*co*-VK) copolymers with 9 (P1), 16 (P2), and 37 mol % (P3) of VK units in a photoinert PMMA matrix. Excitation 300 nm. The blue curve is the original spectrum. The red curve is cumulative as the sum of the individual green peaks obtained by deconvolution using Equation 2 (see the main paper text). The calculation was performed in OriginPro [1].

Based on the parameters obtained in the deconvolution of the luminescence spectra, the contributions to the emission spectra of various photoprocesses related to the photoluminescence of BK monomers, high-energy and low-energy excimers [VK···VK]* were calculated. The calculations are presented in Table S1.

Table S1. Parameters of photoluminescence and excitation electronic energy transferring (EET) rate in photoprocesses in PMMA films containing the MPC based on Tb^{3+} and poly(VT-*co*-VK).

Copolymer	VK unit content, mol. %	VK unit luminescence contribution $\%I_M$, %	Tb^{3+} luminescence contribution $\%I_{Tb(III)}$, %	Tb^{3+} luminescence EET rate $\%I_{Tb(III)}$ / $\%I_M$	Tb^{3+} luminescence intensity @543 nm $I_{543b(III)}$, arb. u.	Excimer contribution $\%I_{E^*}$, %	Excimer EET rate $\%I_{E^*}$ / $\%I_M$
P1	9	27.30	11.93	0.44	223	60.76	2.23
P2	16	16.34	8.50	0.52	251	75.16	4.60
P3	37	7.30	3.01	0.41	81	89.69	12.30

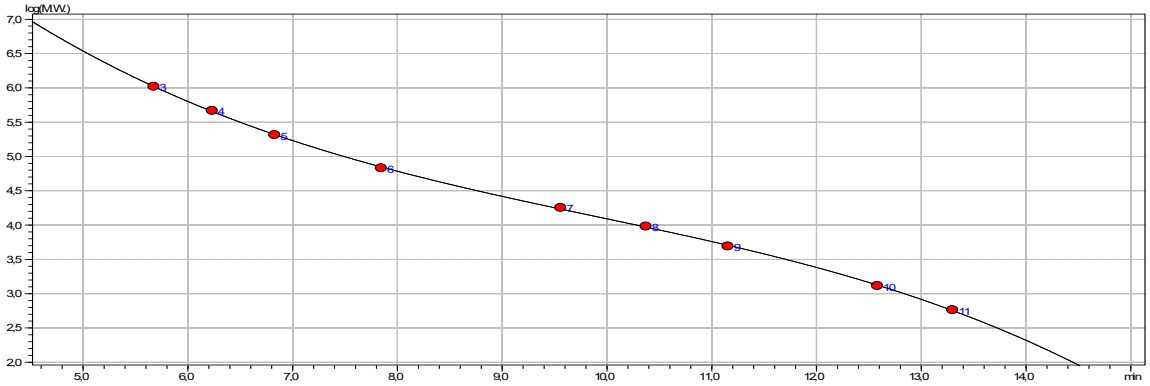


Figure S2. Calibration curve for size-exclusion chromatography. R^2=0,998.

References

1. OriginPro, Version 2023 (built 10.0.0.154). OriginLab Corporation, Northampton, MA, USA.