Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

$Ru(bpy)_3^{2+}$ Derivatized Polystyrenes Constructed by Nitroxide-Mediated Radical Polymerization. Relationship Between Polymer Chain Length, Structure and Photophysical Properties†

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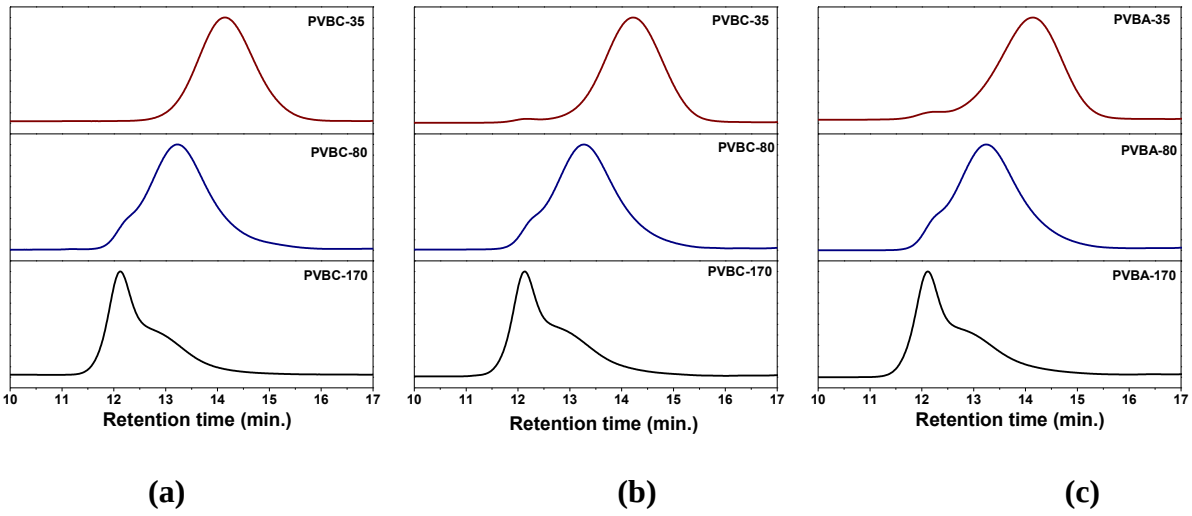

Figure S1. GPC elution curve of (a) PVBC-n-NMP, (b) PVBC-n and (c) PVBA-n in THF

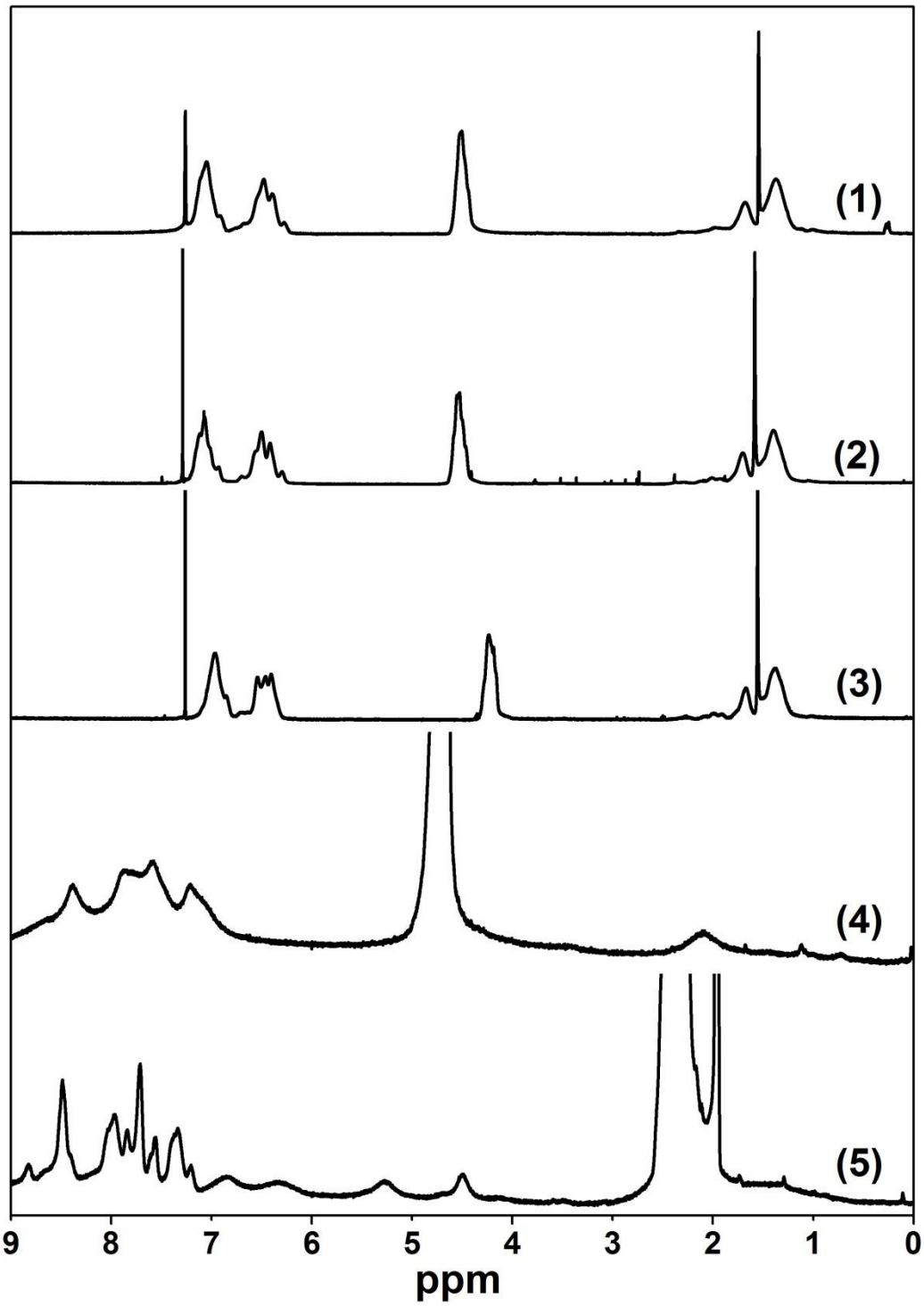

Figure S2. ^{1}H NMR spectra of (1) PVBC-170-NMP, (2) PVBC-170 and (3) PVBA-170 in $CDCl_3$, (4) PS_{170}-Ru(Cl) in D_2O, and (5) PS_{170}-Ru(PF_6) in CD_3CN

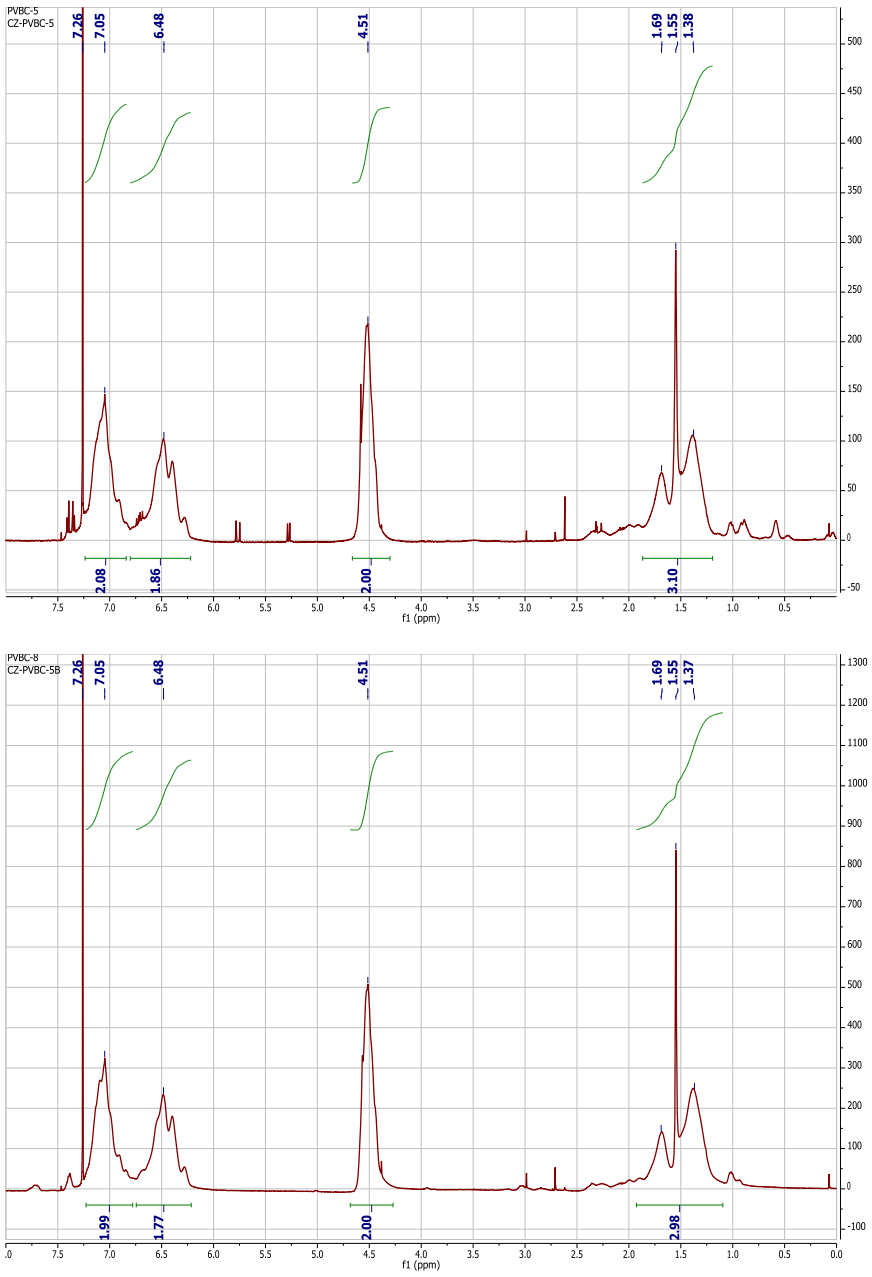

Figure S3. ^{1}H NMR spectra of PVBC-35-NMP (top), and PVBC-35 (bottom) in $CDCl_3$.

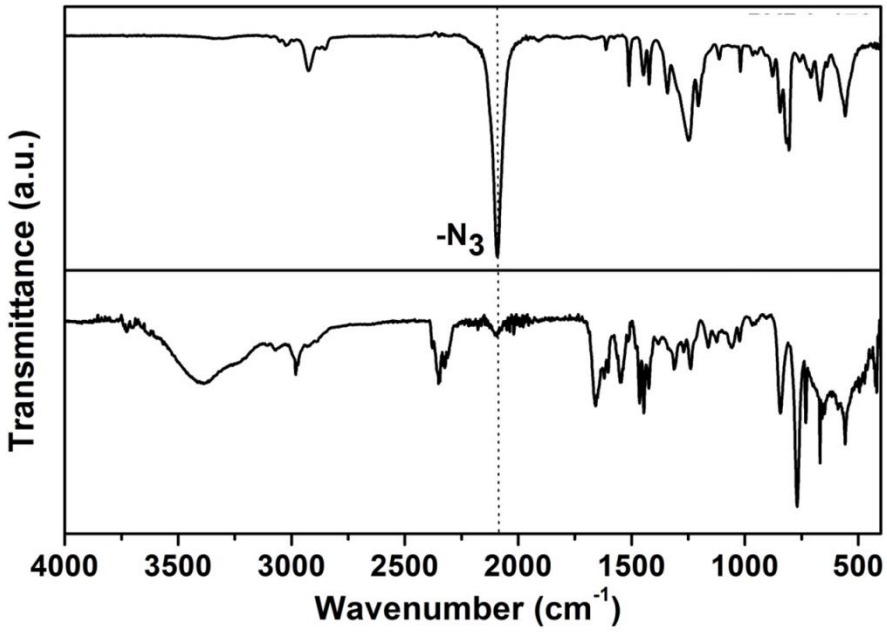

Figure S4. ATR-IR spectra of (top) PVBA-170 and (bottom) PS_{170}-Ru(Cl).

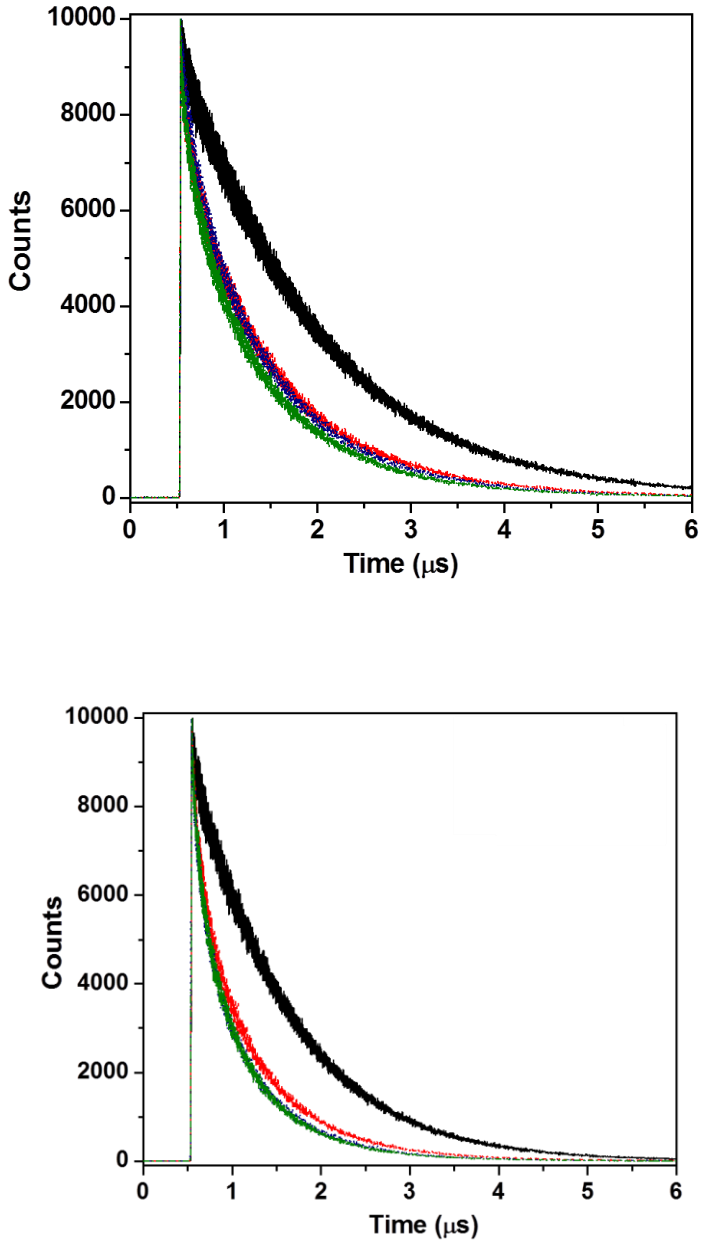

Figure S5. Emission decay profiles of (top) Ru(PF_6) (black), PS_{35}-Ru(PF_6) (red), PS_{80}-Ru(PF_6) (navy), and PS_{170}-Ru(PF_6) (olive) in degassed CH_3CN and (bottom) Ru(Cl) (black), PS_{35}-Ru(Cl) (red), PS_{80}-Ru(Cl) (navy), and PS_{170}-Ru(Cl) (olive) in degassed methanol.

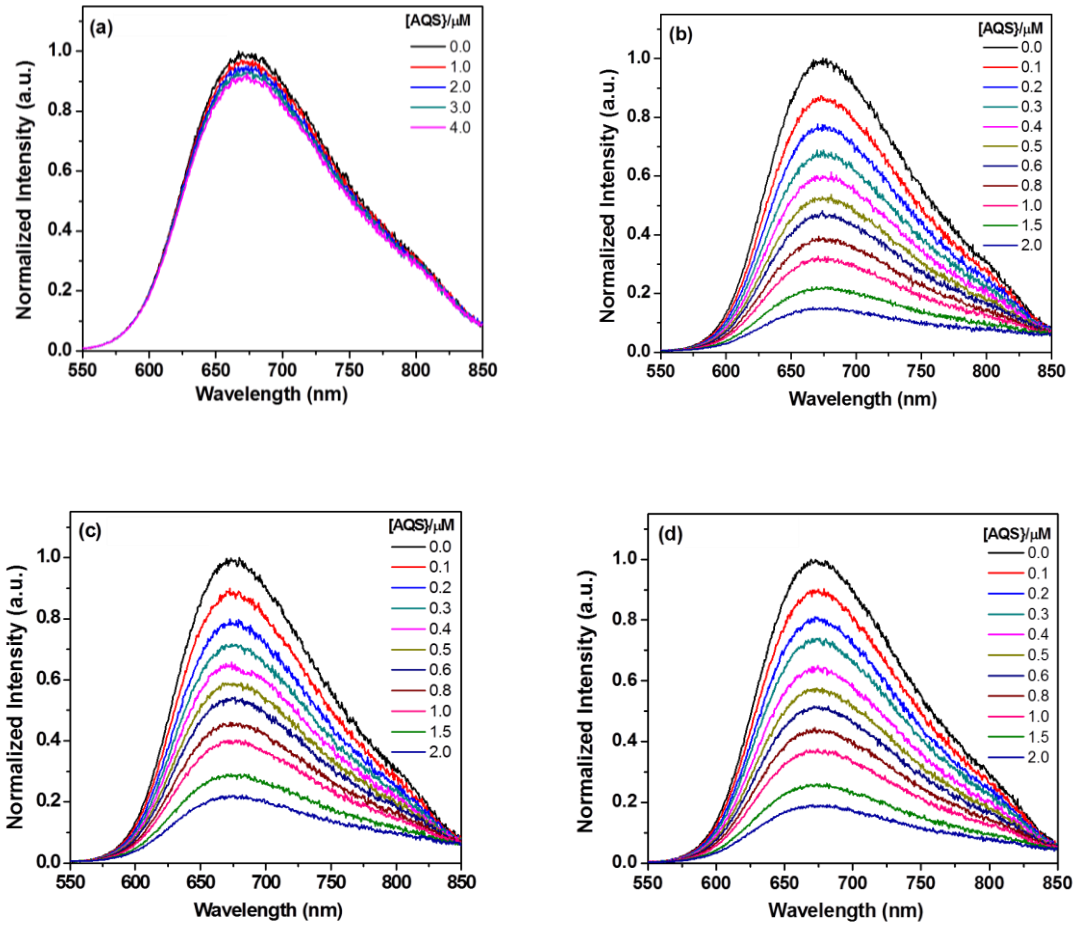

Figure S6. Emission quenching of (a) Ru(Cl), (b) PS_{35}-Ru(Cl) , (c) PS_{80}-Ru(Cl) , and (d) PS_{170}-Ru(Cl) (c = 10 μM) by AQS (c = 0 – 2 μM) in degassed aqueous solution.

Table S1. PS_{20}-Ru (20 repeat units) studied using UFF MD. All simulation cells include the polymer, 20 Cl^- ions, and solvent molecules.

Name	Tacticity	Solvent	# of solvent molecules	Average nearest-neighbor Ru-Ru distance/Å	Shortest Ru-Ru distance from g(r)/Å
P1	Atactic	acetonitrile	1072	10.78 ± 1.73	7.8
P2	Syndiotactic	acetonitrile	1072	10.81 ± 1.70	7.8
P3	Isotactic	acetonitrile	1023	10.56 ± 1.81	7.7
P1'	Atactic	CH_3OH	1373	10.57 ± 2.19	7.5
P2'	Syndiotactic	CH_3OH	1373	11.08 ± 1.32	8.1
P3'	Isotactic	CH_3OH	1310	11.19 ± 1.40	7.9

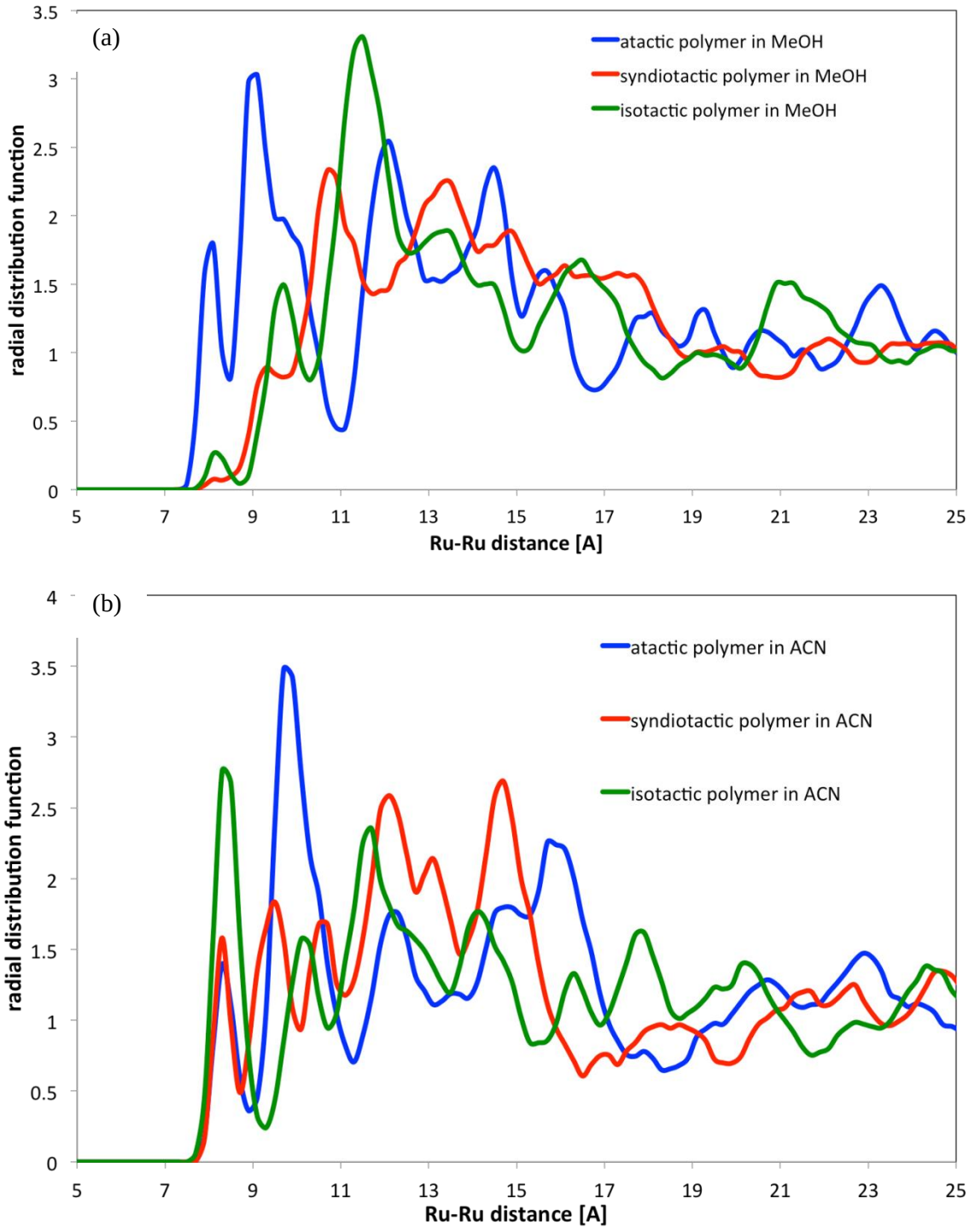

Figure S7. Variations in radial distribution function, g(r), for Ru-Ru distances for different PS_{20}-Ru (20 repeat units) tacticities (atactic polymer in blue, syndiotactic in red, and isotactic polymer in green) in (a) acetonitrile and (b) methanol.

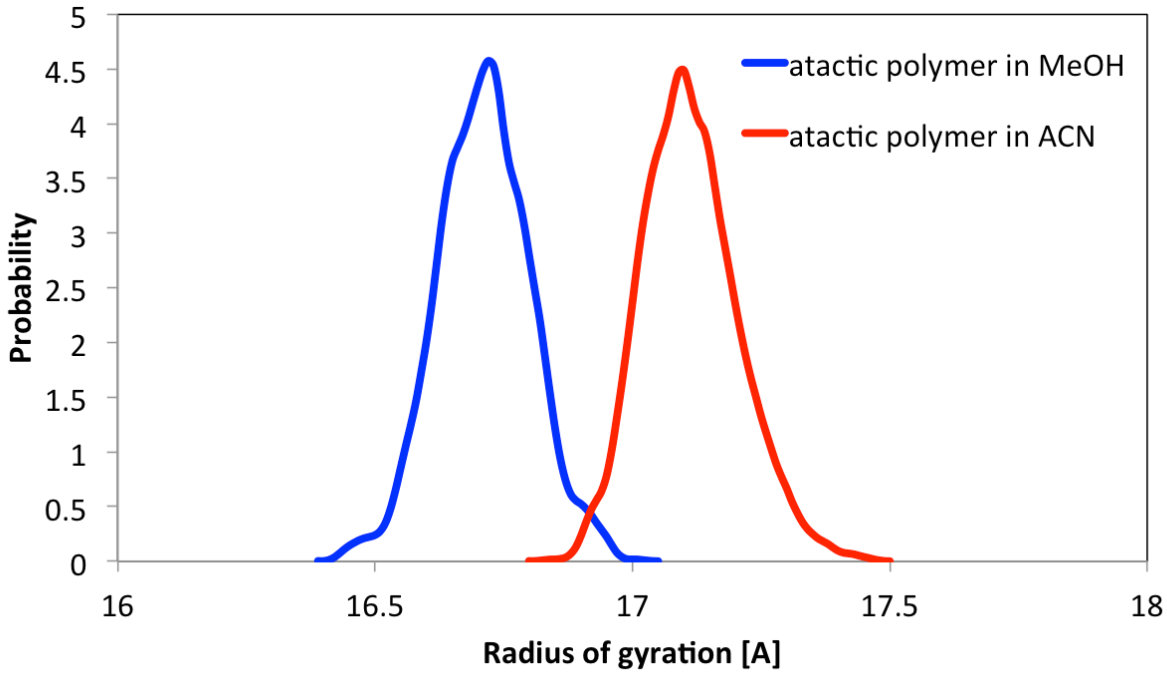

Figure S8. Atactic PS_{20}-Ru (20 repeat units) solvated in methanol (blue line, maximum is at 16.71 Å) has a smaller radius of gyration than in acetonitrile (red line, maximum is at 17.09 Å).

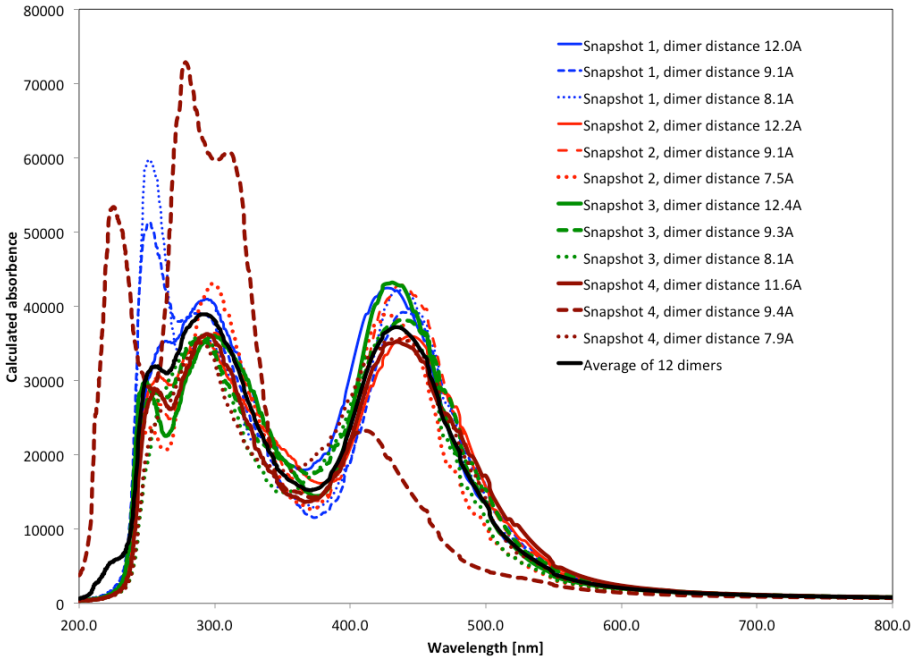

Figure S9. TD-DFT calculated electronic excitations for 12 polypyridylruthenium dimers, as well as the average of all 12 spectra.

Table S2. Which atoms contributed to orbitals that participate in calculated UV-Vis excitations for 3 dimers with different Ru-Ru distances. The atoms are named according to the center, i.e. Ru1 is the Ru atom in monomer 1, while Ru2 is the Ru atom in the 2nd monomer in the dimer. Bpy2B is the bpy unit in monomer 2 that is the bridge to the polymer backbone, and bpy21 and bpy22 are the other bpy units in monomer 2. The only case where there are excitations between monomers is when the two monomers are close by (7.5A).

Excitation [nm]	Strength [calculated]	Atoms that contribute to the orbitals that participate in the excitation
Snapshot 2, dimer distance 12.2A		
469.5	0.16	Ru2(74%)-->bpy2B(76%)
450.5	0.13	Ru1(73%)-->bpy1B(75%)
444.4	0.10	Ru2(74%)-->bpy22(71%)
427.4	0.10	Ru1(73%)-->bpy12(44%), bpy11(44%)
319.5	0.05	Ru1(73%)-->bpy12(45%), bpy11(42%)
289.0	0.16	bpy2B(47%)-->bpy2B(82%)
281.7	0.05	bpy2B(74%)-->bpy2B(88%)
Snapshot 2, dimer distance 9.1A		
463.0	0.09	Ru2(49%)-->bpy2B(63%)
456.6	0.12	Ru1(56%)-->bpy1B(73%)
454.5	0.06	Ru2(64%)-->bpy22(40%), bpy21(34%)
444.4	0.09	Ru2(59%)-->bpy22(41%), bpy21(36%)
436.7	0.10	Ru1(71%)-->bpy12(44%), bpy11(37%)
434.8	0.12	Ru2(57%)-->bpy21(46%), bpy22(38%)
316.5	0.07	Ru2(72%)-->bpy21(34%)
285.7	0.07	bpy11(43%)-->bpy1B(78%)
Snapshot 2, dimer distance 7.5A		
467.3	0.10	Ru2(71%)-->bpy2B(59%)
456.6	0.13	Ru1(55%)-->bpy1B(41%)
438.6	0.12	Ru2(51%)-->bpy22(32%), bpy21(27%)
431.0	0.06	Ru1(56%)-->bpy12(45%)
330.0	0.08	**Ru1(73%)-->bpy11(27%), bpy21(17%), bpy22(18%)**
294.1	0.09	**bpy2B(43%), Ru2(36.3%)-->bpy2B(35%), bpy11(25%)**