Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

- Supporting Information -

Network Structure in Telechelic Transient Polymer Networks: Extension of the Miller–Macosko's Model

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Table S1. Thermodynamic constants for the complexation of tridentate ligands with various metal ions.

Metal ion	Ligand	Complex	Logβ	Temperature (°C)	Ref.
Cu^{2+}	Arginine	ML_1	7.555	25	(Murphy et al., 2020)
		ML_2	14.007		
	Asparagine	ML_1	7.788	37	
		ML_2	14.142		
	Aspartic acid	ML_1	8.83	25	
		ML_2	15.93		
	Glutamine	ML_1	7.71		
		ML_2	14.12		
	Glutamic acid	ML_1	8.3		
		ML_2	15.03		
	Lysine	ML_1	7.62		
		ML_2	13.94		
	Serine	ML_1	7.748	37	
		ML_2	14.083		
	Threonine	ML_1	7.98	25	
		ML_2	14.66		
	Tyrosine	ML_1	7.9		
		ML_2	15.17		
	(1 ,4,7-triazacyclononanene-N,N,N"-triacetic acid)	ML_1	19.8	25	(Martell et al., 1996)
Fe^{2+}	Arginine	ML_1	3.2	20	
	Asparagine	ML_1	4.37	25	
		ML_2	7.57		
	Aspartic acid	ML_1	5.34		
		ML_2	8.57		
	Glutamic acid	ML_1	3.5	20	(Murphy et al., 2020)
	Lysine	ML_1	4.5		
	Serine	ML_1	4.299		

		ML_2	7.377	20	
	Threonine	ML_1	3.69	40	
		ML_2	6.5		
	Tyrosine	ML_2	7.1	20	
	Terpyridine	ML_1	7.1		(H Holyer et al., 1965)
		ML_2	20.9		
Fe^{3+}	Arginine	ML_1	8.7		
	Asparagine	ML_1	8.6		
	Aspartic acid	ML_1	11.4		
	Glutamic acid	ML_1	13.39		
	Serine	ML_1	9.2		
	Threonine	ML_1	8.6		
	(1 ,4,7-triazacyclononanene-N,N,N"-triacetic acid)	ML_1	28.3	25	(Martell et al., 1996)
Mn^{2+}	Terpyridine	ML_1	4.4		(H Holyer et al., 1965)
Co^{2+}	Terpyridine	ML_1	8.4		
		ML_2	18.3		
	(1 ,4,7-triazacyclononanene-N,N,N"-triacetic acid)	ML_1	17.5		
Ni^{2+}	Terpyridine	ML_1	10.7		(H Holyer et al., 1965)
		ML_2	21.8		
Zn^{2+}	Terpyridine	ML_1	6		
	(1 ,4,7-triazacyclononanene-N,N,N"-triacetic acid)	ML_1	18.3	25	(Martell et al., 1996)
Cd^{2+}	Terpyridine	ML_1	5.1		(H Holyer et al., 1965)
Ga^{2+}	(1 ,4,7-triazacyclononanene-N,N,N"-triacetic acid)	ML_1	31	25	(Martell et al., 1996)
In^{2+}	(1 ,4,7-triazacyclononanene-N,N,N"-triacetic acid)	ML_1	26.2		

Table S2. Thermodynamic constants for the complexation of tridentate ligands with various metal ions.

Metal ion	Ligand	Complex	Logβ	Temperature (°C)	Ref.
Fe^{3+}	nitrocatechole	ML_1	17.1	Not Reported	(Cazzell & Holten-Andersen, 2019)
		ML_2	30.5		
		ML_3	40		
	Alanine	ML_1	10.98	30	(Murphy et al., 2020)
	Glycine	ML_1	10	25	
	Leucine	ML_1	9.9	20	
	Phenylalanine	ML_1	10.39	25	
		ML_2	19.1		
		ML_3	26		
	Proline	ML_2	10	20	
	Tryptophan	ML_1	9		
	Valine	ML_1	9.6		
Fe^{2+}	Alanine	ML_1	3.54		
	Glycine	ML_1	4.13	25	
		ML_2	7.65		
	Leucine	ML_1	3.42	20	
	Phenylalanine	ML_1	3.74	25	
		ML_2	7.19		
		ML_3	10.7		
	Proline	ML_2	8.3	20	
	Tryptophan	ML_1	3.92	25	
		ML_2	7.39		
		ML_3	9.5		
	Valine	ML_1	3.39	20	
	Bipyridine	ML_1	4.3	25	(H Holyer et al., 1965)
		ML_3	17.5		
	histidine	ML_1	5.88	25	(Murphy et al., 2020)
		ML_2	10.43		
Al^{3+}	nitrocatechole	ML_1	13.74	Not Reported	(Cazzell & Holten-Andersen, 2019)
		ML_2	25.4		
		ML_3	34.3		
Cu^{2+}	alanine	ML_1	8.17	30	(Murphy et al., 2020)
		ML_2	14.94		
Cu^{2+}	Glycine	ML_1	8.07		
		ML_2	14.86		
	Isoleucine	ML_1	8.5	25	
		ML_2	15.79		
	Leucine	ML_1	8.276		
		ML_2	15.174		
	Phenylalanine	ML_1	7.93	25	

		ML_2	14.83		
	Phenanthroline	ML_1	9	25	(Griffith et al., 1965)
		ML_2	15.7		
		ML_3	20.7		
	Bipyridine	ML_1	8		
	Histidine	ML_1	9.75	37	(Murphy et al., 2020)
		ML_2	17.49		
	Proline	ML_1	8.6	25	
		ML_2	15.09		
	Tryptophan	ML_1	8.02		
		ML_2	15.56		
	Valine	ML_1	8.05	30	
		ML_2	14.91		
Cu^+	alanine	ML_1	9.6	25	
	Glycine	ML_1	10		
	histidine	ML_1	12.8		
		ML_2	25.2		
Mn^{2+}	Phenanthroline	ML_1	3.6	25	(Griffith et al., 1965)
	Bipyridine	ML_1	2.6	25	(H Holyer et al., 1965)
Co^{2+}	Phenanthroline	ML_1	7.2		
	Bipyridine	ML_1	5.7		
		ML_3	16.1		
	4,4 dimethyl 2,2 bipyridyl	ML_1	6.4	25	(Martell & Smith, 1989)
		ML_2	11.3		
		ML_3	16.6		
Ni^{2+}	Bipyridine	ML_1	7.1	25	(H Holyer et al., 1965)
	Bipyridine	ML_2	12.1	25	(Griffith et al., 1965)
	Bipyridine	ML_3	20.1	25	(H Holyer et al., 1965)
	histidine	ML_1	6.78	Not Reported	(Cazzell & Holten-Andersen, 2019)
		ML_2	11.78		
		ML_3	14.9		
Zn^{2+}	Phenanthroline	ML_1	5.7	25	(Griffith et al., 1965)
	2,2 -Bipyridyl	ML_1	5.12	25	(Martell & Smith, 1989)
		ML_2	9.63		
		ML_3	13.3		
Cd^{2+}	Bipyridine	ML_1	4.3	25	(H Holyer et al., 1965)
	Phenanthroline	ML_1	5.4	25	(Griffith et al., 1965)
	2,2 -Bipyridyl	ML_1	4.22	25	(Martell & Smith, 1989)
		ML_2	7.8		
		ML_3	10.4		
Hg^{2+}	Bipyridine	ML_1	9.6	25	(Griffith et al., 1965)

Ag^{2+}	Phenanthroline	ML_1	5		
		ML_2	7		

Table S3. Thermodynamic constants for the complexation of monodentate ligands with various metal ions.

Metal ion	Ligand	Complex	Logβ	Temperature (°C)	Ref.
Ni^{2+}	Pyridine	ML_1	2.1	25	(Griffith et al., 1965)
	Pyridine	ML_1	1.88	25	(Martell & Smith, 1989)
		ML_2	4.98		
		ML_3	8.58		
		ML_4	11.98		
	1-methyl Imidazole	ML_1	3.05	25	(Aruga, 1983)
	Pyrazole	ML_1	1.8	25	(Martell & Smith, 1989)
		ML_2	5.1		
		ML_3	9.3		
		ML_4	13.9		
	1-Ethylimidazole	ML_1	3.04		
		ML_2	8.54		
		ML_3	16.04		
		ML_4	25.04		
		ML_5	34.84		
		ML_6	45.04		
	1-Propylimidazole	ML_1	3.06		
		ML_2	8.66		
		ML_3	16.26		
		ML_4	25.46		
		ML_5	35.76		
		ML_6	46.76		
Co^{2+}	1-methyl Imidazole	ML_1	2.4	25	(Aruga, 1983)
	1-methyl Imidazole	ML_2	6.54	25	(Martell & Smith, 1989)
		ML_3	11.86		
		ML_4	18.56		
	Pyridine	ML_1	1.2	25	
		ML_2	2.95		
		ML_3	4.75		
		ML_4	6.35		
	Pyrazole	ML_1	1.3		
		ML_2	3.6		
		ML_3	6.5		

		ML_4	9.7		
	1-Ethylimidazole	ML_1	2.32		
		ML_2	6.52		
		ML_3	11.92		
		ML_4	18.92		
		ML_5	26.32		
	1-Propylimidazole	ML_1	2.38		
		ML_2	6.58		
		ML_3	11.98		
		ML_4	18.88		
		ML_5	26.78		
		ML_6	35.18		
Zn^{2+}	1-methyl Imidazole	ML_1	2.7	25	(Aruga, 1983)
	Pyridine	ML_1	1.08	25	(Martell & Smith, 1989)
		ML_2	2.58		
		ML_3	4.18		
		ML_4	5.58		
	Pyrazole	ML_1	1.1		
		ML_2	3		
		ML_3	5.5		
		ML_4	8.2		
	1-Ethylimidazole	ML_1	2.5		
		ML_2	7.3		
		ML_3	14.7		
		ML_4	24		
	1-Propylimidazole	ML_1	2.62		
		ML_2	7.32		
		ML_3	14.52		
		ML_4	23.72		
		ML_5	33.72		
Cu^{2+}	1-methyl Imidazole	ML_1	4.3	25	(Aruga, 1983)
	Pyridine	ML_1	2.54	25	(Martell & Smith, 1989)
		ML_2	6.94		
		ML_3	12.64	25	
		ML_4	19.04		
	Hydrogen azid	ML_1	2.86	25	
		ML_2	5.42		
		ML_3	9.9		
		ML_4	16.01		
	Pyrazole	ML_1	2.33		
		ML_2	6.53		

		ML_3	12.23		
		ML_4	18.83		
	1-Ethylimidazole	ML_1	4.4		
		ML_2	12.4		
		ML_3	23.4		
		ML_4	36.6		
		ML_5	50.08		
	1-Propylimidazole	ML_1	4.25		
		ML_2	12.05		
		ML_3	22.75		
		ML_4	35.85		
		ML_5	50.5		
Fe^{3+}	Hydrogen azid	ML_1	4.51		
		ML_2	7.48		
		ML_3	9.58		
		ML_4	10.95		
		ML_5	11.8		
Fe^{2+}	Pyrazole	ML_1	0.8	25	
		ML_2	1.9		
		ML_3	3.2		
		ML_4	4.7		
Cd^{2+}	Pyrazole	ML_1	1.1		
		ML_2	2.7		
		ML_3	4.5		
In^{2+}	Hydrogen azide	ML_1	3.19		
		ML_2	5.61		
		ML_3	7.26		
		ML_4	8.46		
Th^{4+}	picolinic acid-N-oxide	ML_1	4.4	25	(Dumpala et al., 2018)
		ML_2	7.69		
		ML_3	10.46		
		ML_4	12.08		

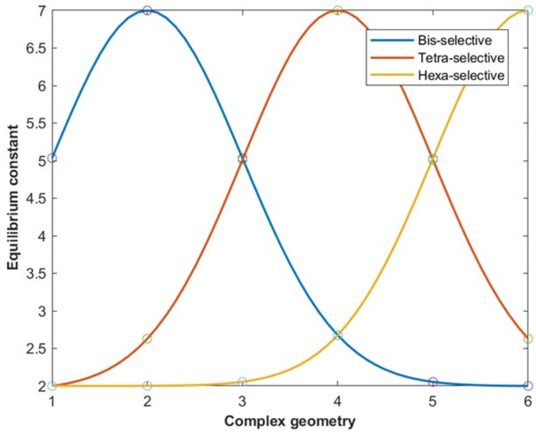

Figure S1. Definition of the equilibrium constant, on the log scale, as a continuous function of the complex geometry for a metal–ligand combination capable of forming up to six coordinative bonds: the representative distributions are shown for a bis-, tetra-, and a hexa-selective system. The discrete logK$_i$ values used in the modeling for each distribution of logK curves are shown by open circles.

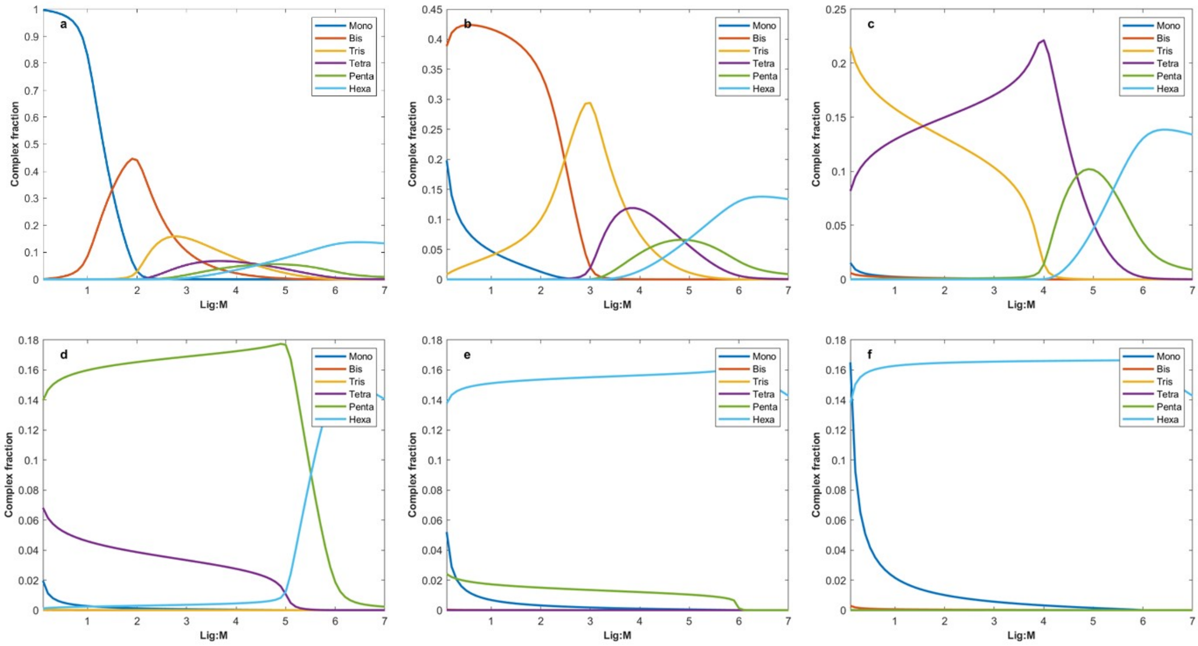

Figure S2. Composition of various complexes ($[ML_i]/[L]_0$) as denoted in the legend for (a) mono-, (b) bis-, (c) tris-, (d) tetra-, (e) penta-, and (f) hexa-selective system.

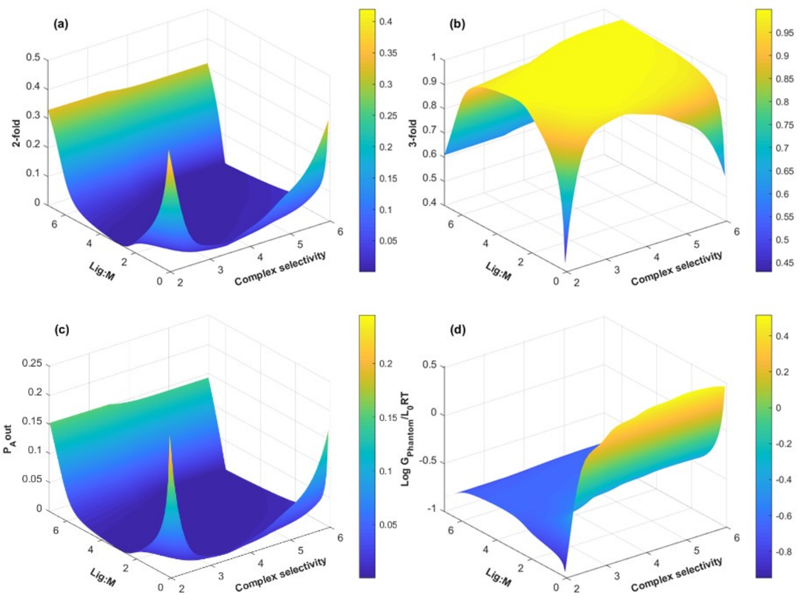

Figure S3. Fraction of (a) 2-fold and (b) 3-fold connected tri-arm polymer precursors in combination with a complex that forms up to 6 transient bonds; the corresponding (c) probability of being connected to a finite network, and (d) logarithm of the normalized modulus.

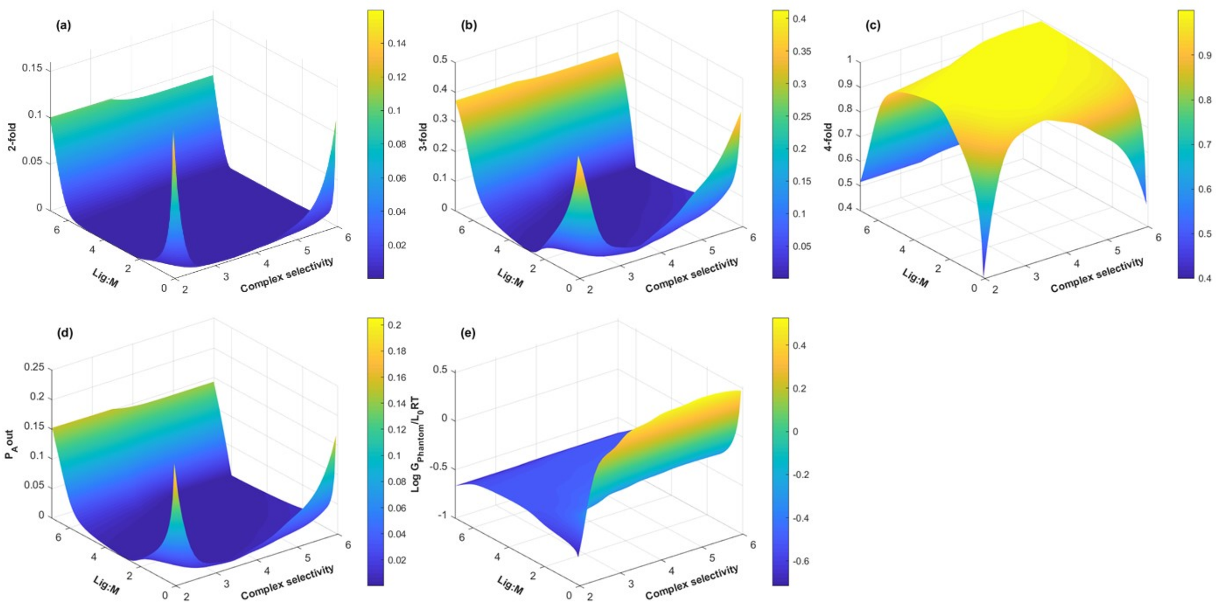

Figure S4. Fraction of (a) 2-fold, (b) 3-fold, and (c) 4-fold connected tetra-arm polymer precursors in combination with a complex that forms up to 6 transient bonds; the corresponding (d) probability of being connected to a finite network, and (e) logarithm of the normalized modulus.

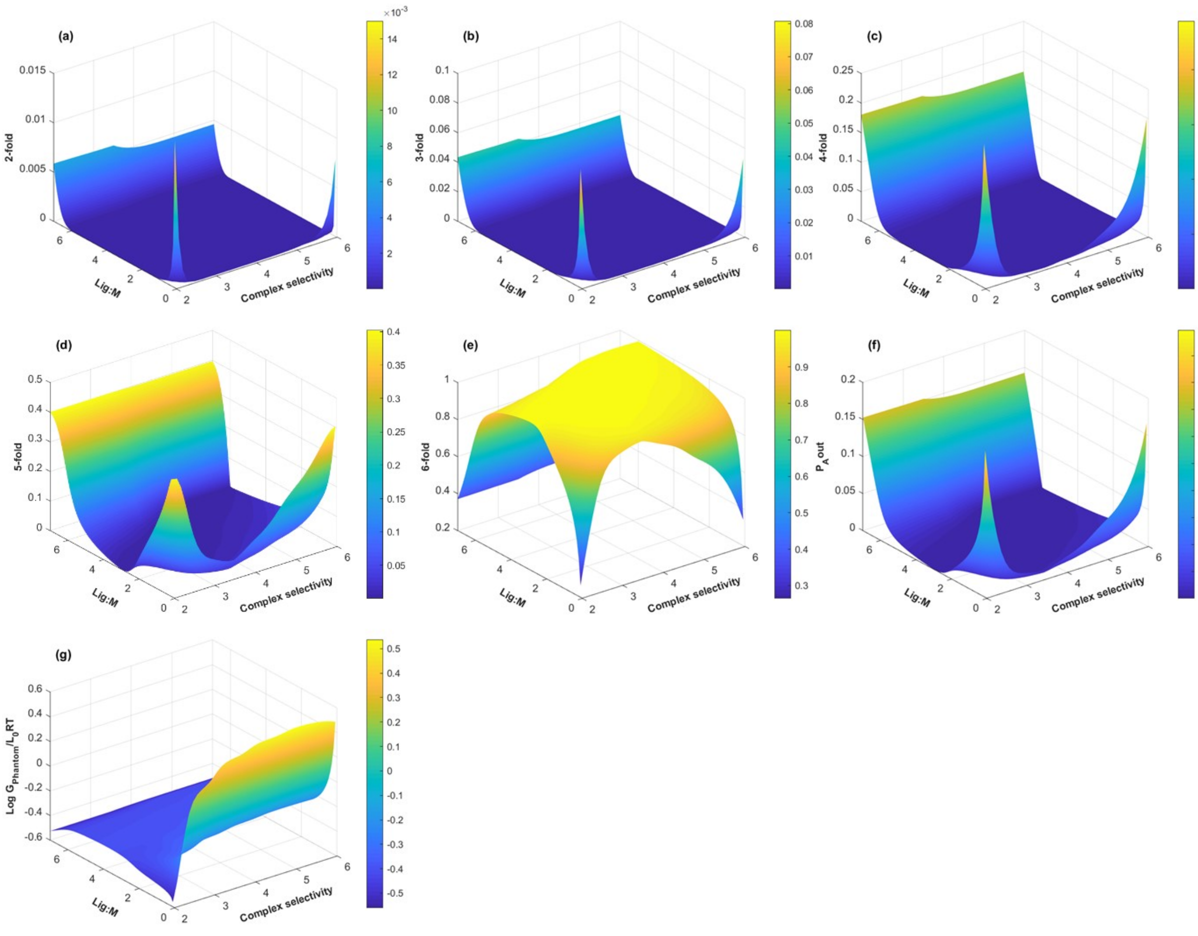

Figure S5. Fraction of (a) 2-fold, (b) 3-fold, (c) 4-fold, (d) 5-fold, and (e) 6-fold connected hexa-arm polymer precursors in combination with a complex that forms up to 6 transient bonds; the corresponding (f) probability of being connected to a finite network, and (g) logarithm of the normalized modulus.

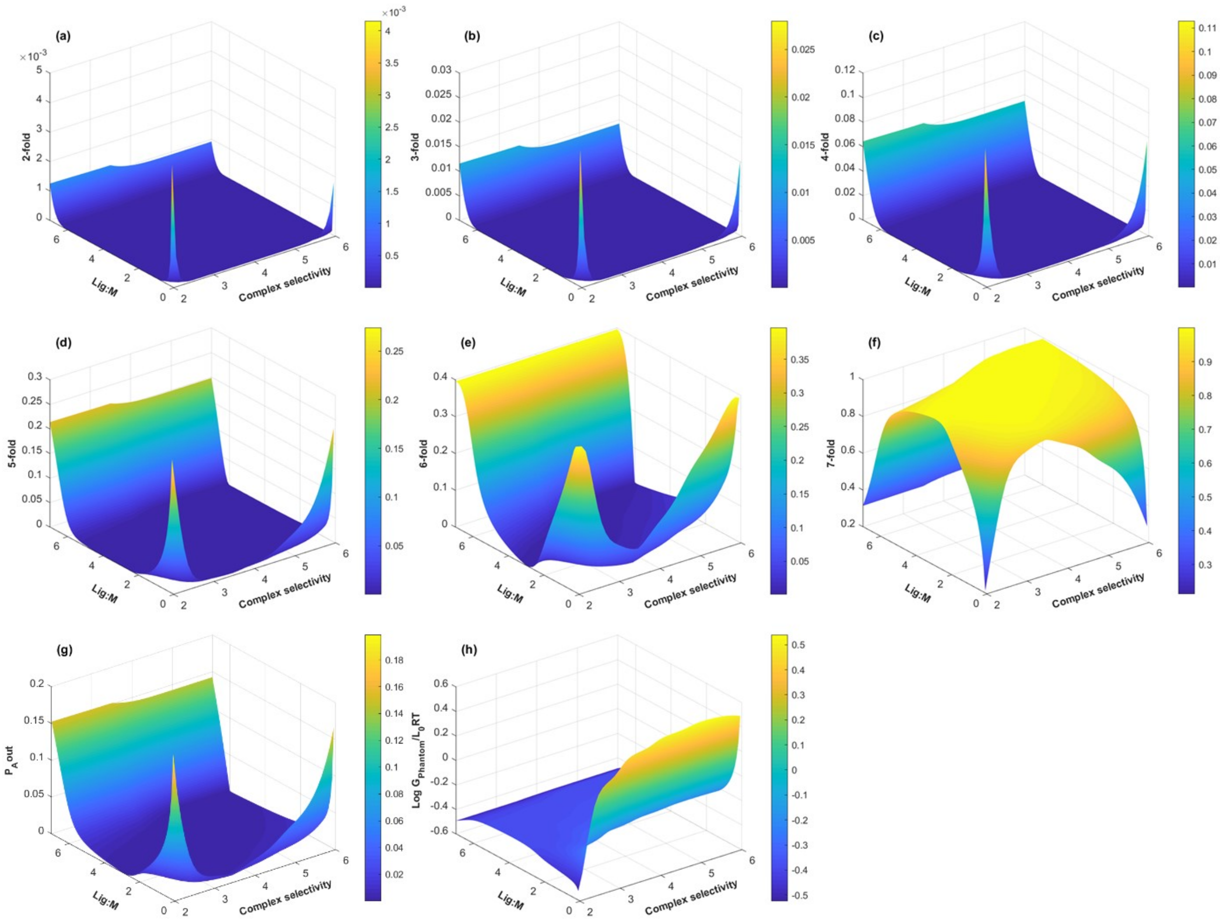

Figure S6. Fraction of (a) 2-fold, (b) 3-fold, (c) 4-fold, (d) 5-fold, (e) 6-fold, and (f) 7-fold connected hepta-arm polymer precursors in combination with a complex that forms up to 6 transient bonds; the corresponding (g) probability of being connected to a finite network, and (h) logarithm of the normalized modulus.

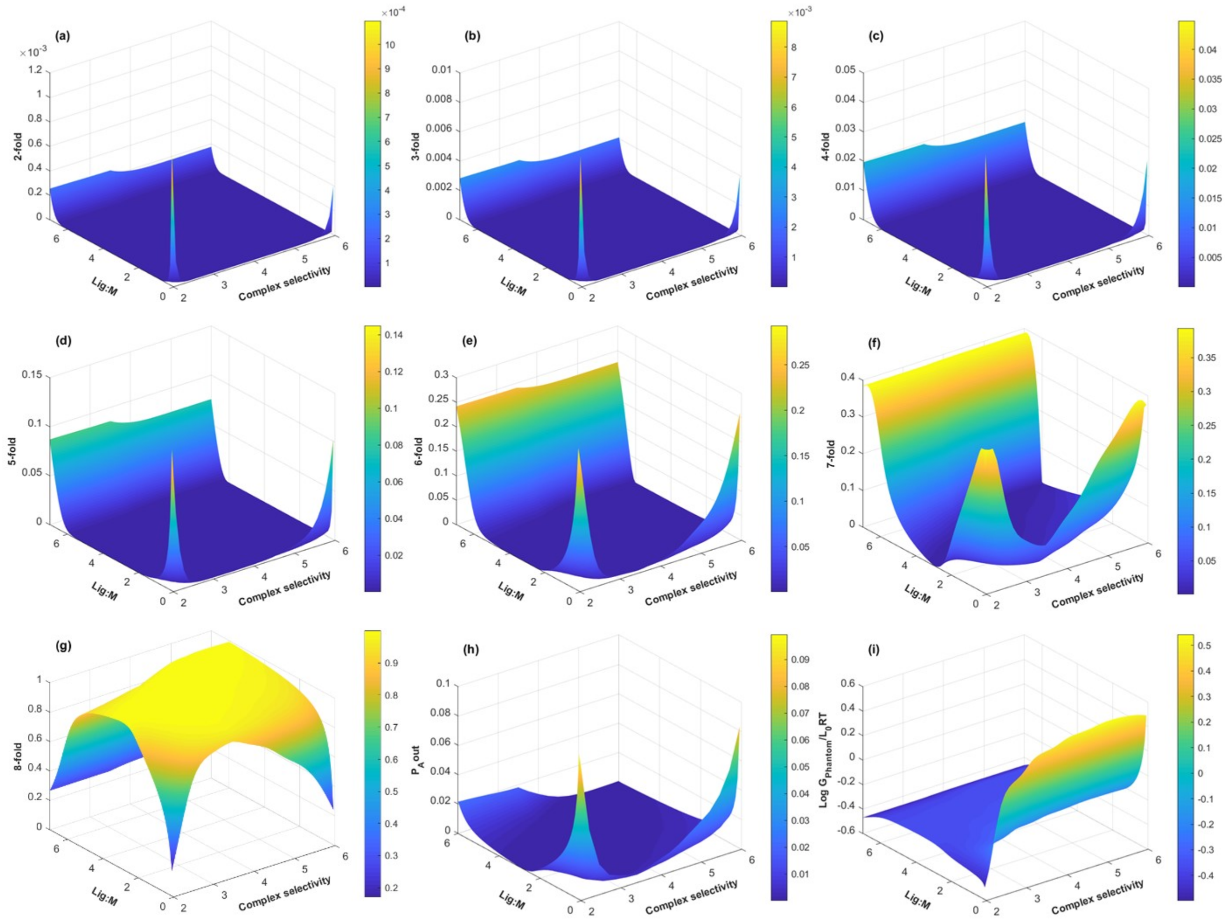

Figure S7. Fraction of (a) 2-fold, (b) 3-fold, (c) 4-fold, (d) 5-fold, (e) 6-fold, (f) 6-fold, and (g) 7-fold connected hepta-arm polymer precursors in combination with a complex that forms up to 6 transient bonds; the corresponding (h) probability of being connected to a finite network, and (i) logarithm of the normalized modulus.

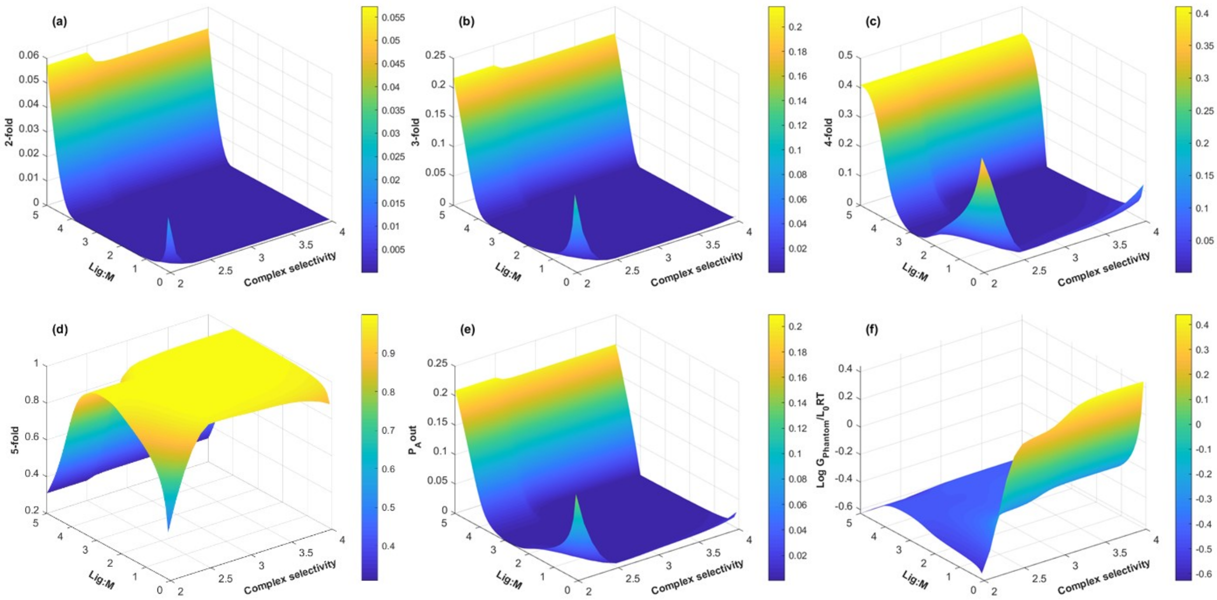

Figure S8. Fraction of (a) 2-fold, (b) 3-fold, (c) 4-fold, (d) 5-fold connected penta-arm polymer precursors in combination with a complex that forms up to 4 transient bonds; the corresponding (e) probability of being connected to a finite network, and (f) logarithm of the normalized modulus.

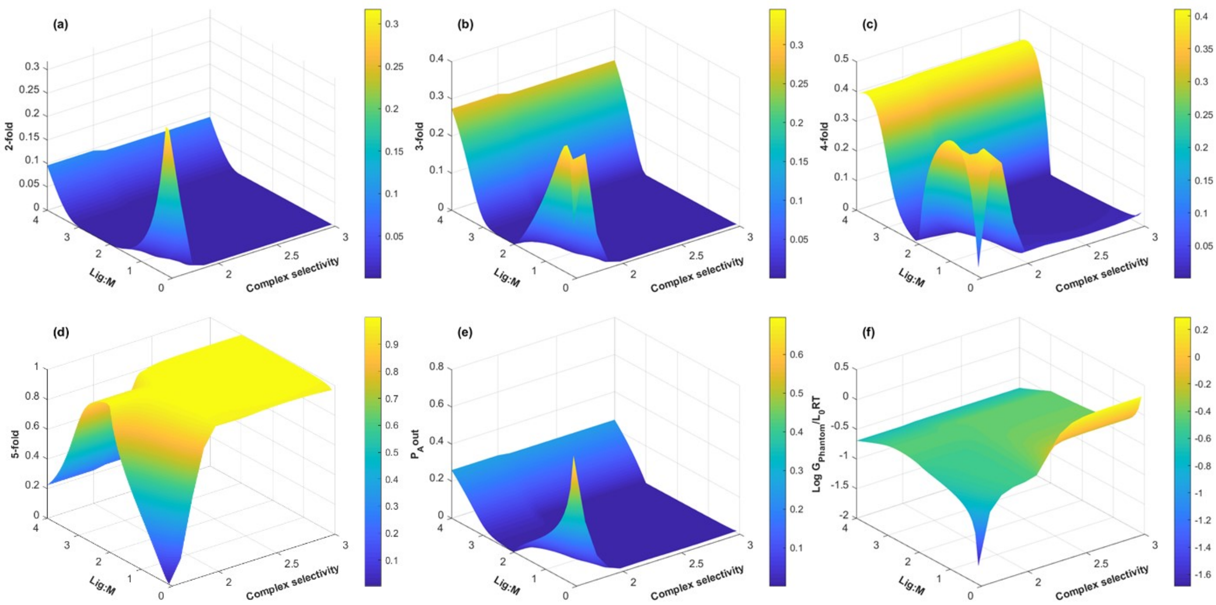

Figure S9. Fraction of (a) 2-fold, (b) 3-fold, (c) 4-fold, (d) 5-fold connected penta-arm polymer precursors in combination with a complex that forms up to 3 transient bonds; the corresponding (e) probability of being connected to a finite network, and (f) logarithm of the normalized modulus.

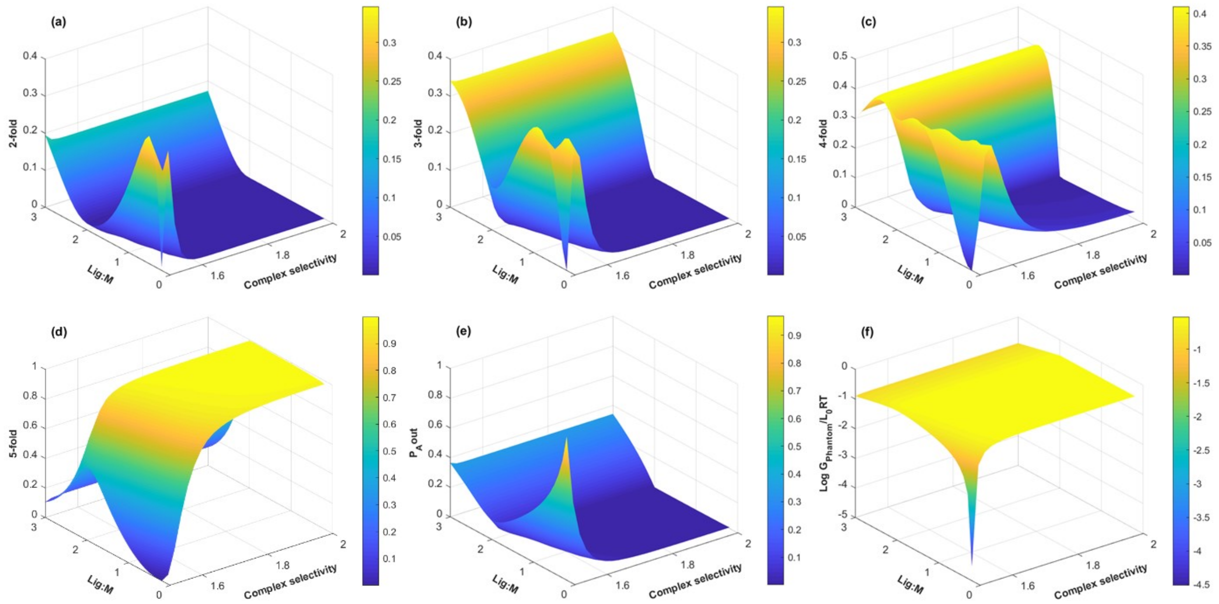

Figure S10. Fraction of (a) 2-fold, (b) 3-fold, (c) 4-fold, (d) 5-fold connected penta-arm polymer precursors in combination with a complex that forms up to 2 transient bonds; the corresponding (e) probability of being connected to a finite network, and (f) logarithm of the normalized modulus.

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