4-(4-chloro-2-oxo-3(1*H*-phenanthro[9,10-*d*]imidazol-2-yl)-2*H*-chromen-6-yl)benzaldehyde as fluorescent probe for medical imaging: linear and nonlinear optical properties

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Supporting informations

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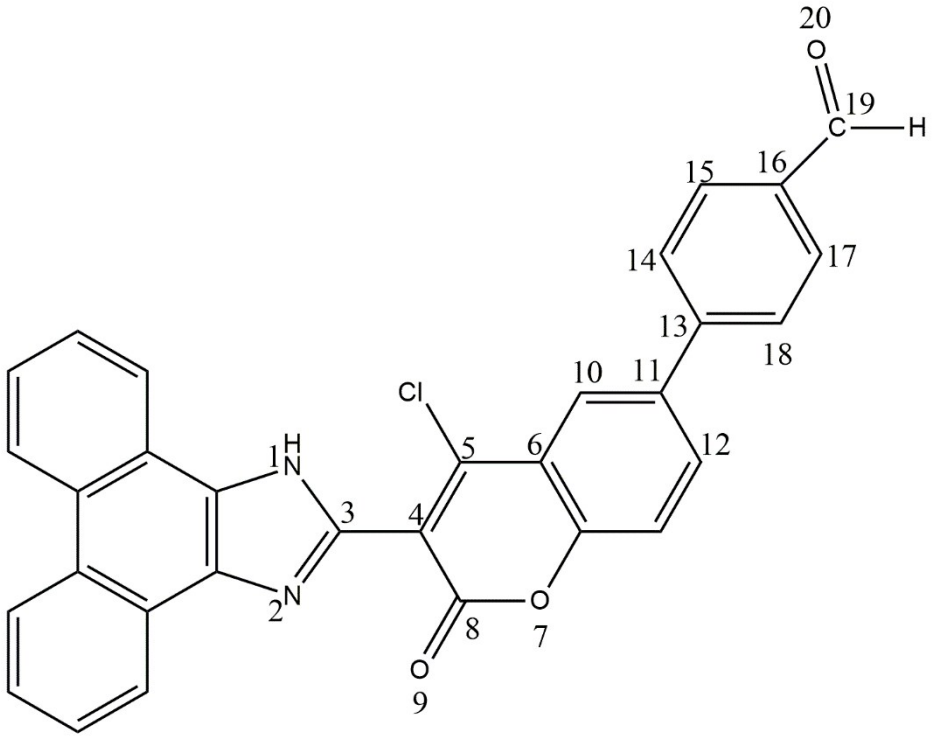

Figure.S1. B5 structure and atom numbering scheme

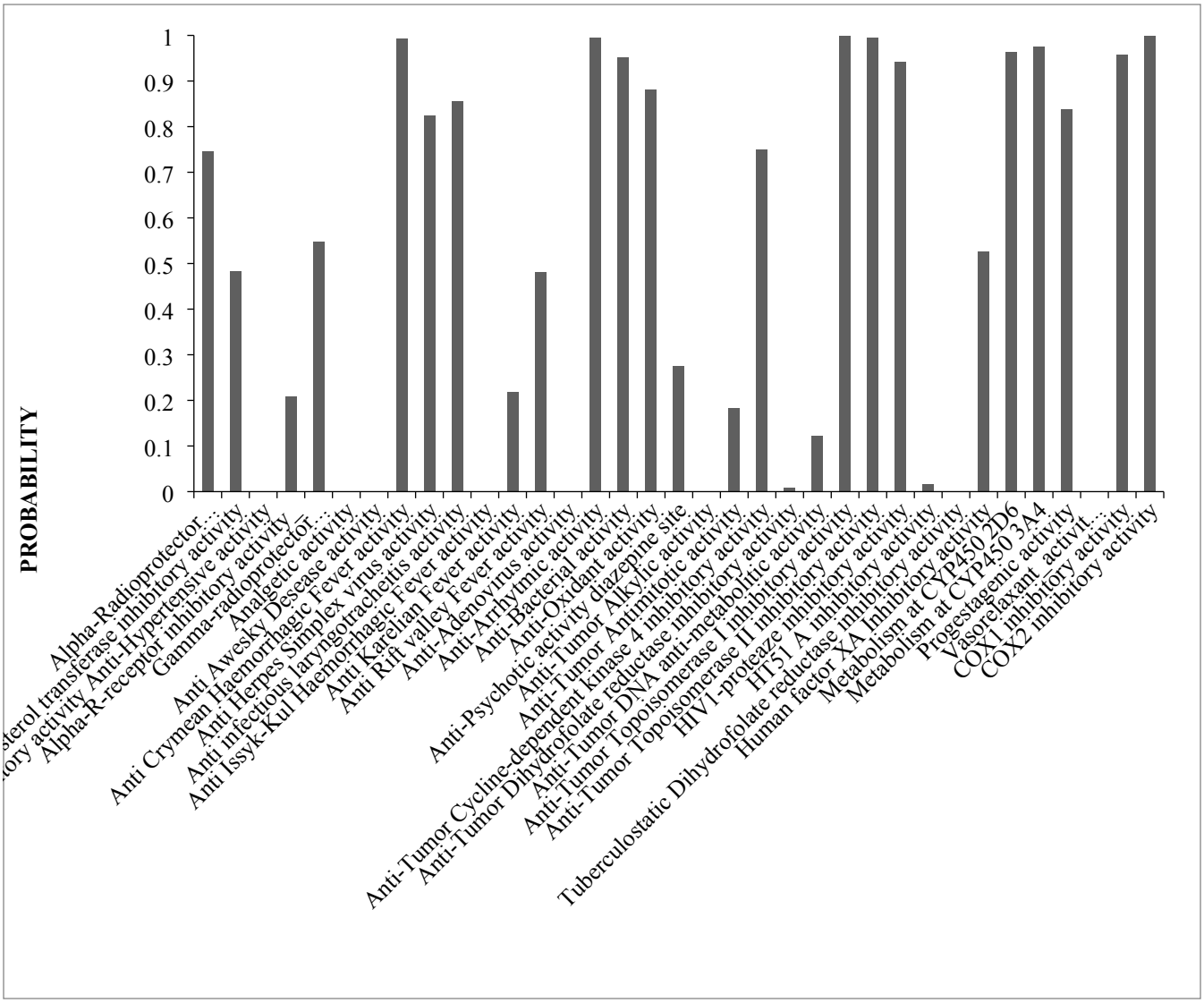

Fig. S2. Biological activities of PB5

	MCH		MeCN		Water	
	S_{GS}	S_{CT}	S_{GS}	S_{CT}	S_{GS}	S_{CT}
bond lengths						
C3-C4	1.45931	1.45777	1.47152	1.44128	1.47152	1.44127
C8=09	1.21058	1.23168	1.20521	1.21591	1.20521	1.21591
C11-C13	1.47740	1.47624	1.47736	1.47674	1.47736	1.47674
C16-C19	1.47314	1.47007	1.46980	1.46740	1.46980	1.46740
C9=O20	1.20909	1.21502	1.21329	1.21446	1.21329	1.21446
bond angles						
N1-C3-C4	121.98810	120.01832	122.34322	122.39795	122.34319	122.39796
N2=C3-C4	126.77114	128.16651	125.29345	126.67344	125.29347	126.67346
C4-C8=O9	125.55265	127.31915	125.25254	128.37398	125.25257	128.37041
C10=C11-C13	120.56803	120.36123	120.69862	120.56563	120.69860	120.56564
C12-C11-C13	120.70975	120.62121	120.79112	120.37284	120.79111	120.37283
C16-C19=O20	124.78455	125.03446	124.84801	125.00442	124.84806	125.00442
C17-C16-C19	119.59626	121.05523	121.22832	121.34229	119.23975	121.34229
dihedral angles						
N1-C3-C4=C5	1.11586	-5.88308	-179.87384	-37.75780	-79.87382	-37.75768
2N=C3-C4-C8	1.31115	-5.52018	-78.94084	-40.15056	-78.94085	-40.15064
C3-C4-C8=O9	-0.50960	3.51167	-1.40874	0.60578	-1.40873	0.60585
C10=C11-C13-C14	-38.50709	-36.95047	-37.48446	-34.49489	-37.48446	-34.49496
C12-C11-C13=C18	-38.57817	-36.50708	-37.52984	-34.93338	-37.52988	-34.93331
C15-C16-C19=O20	-0.15116	-0.21091	-0.23169	-0.27652	-0.23168	-0.27652

Table S1. Selected structural parameters of PB5

	MCH		MeCN		Water	
	S_{GS}	S_{CT}	S_{GS}	S_{CT}	S_{GS}	S_{CT}
bond lengths						
C3-C4	1.45993	1.45442	1.47118	1.43916	1.47118	1.46749
C8=09	1.21170	1.23224	1.20584	1.21590	1.20584	1.20029
C11-C13	1.47824	1.47861	1.47848	1.47904	1.47849	1.47880
C16-C19	1.50623	1.50580	1.50504	1.50480	1.50504	1.47594
bond angles						
N1-C3-C4	121.98551	120.18401	122.61558	122.47774	122.61271	122.91209
N2=C3-C4	126.74493	128.06860	125.06129	126.68564	125.06429	124.92078
C4-C8=O9	125.47657	127.15024	125.20896	128.27825	125.20885	125.47646
C10=C11-C13	120.79812	120.57093	120.87916	120.70627	120.88029	120.72410
C12-C11-C13	120.72440	120.60179	120.85509	120.45887	120.85344	120.87351
C17-C16-C19	120.76489	120.87795	120.70459	120.73440	120.70227	120.75263
dihedral angles						
N1-C3-C4=C5	-3.53231	7.32563	-77.86610	-36.28595	-77.86079	-58.65953
2N=C3-C4-C8	-4.22226	6.60816	-76.25312	-38.84144	-76.24509	-58.07061
C3-C4-C8=O9	1.75996	-4.21328	-1.94206	1.03830	1.94202	-5.13806
C10=C11-C13-C14	-39.21754	-38.89596	-37.95016	-35.42616	-37.94965	-39.63393
C12-C11-C13=C18	-38.84864	-38.33781	-38.05373	-35.71382	-38.04951	-39.71552

Table S2. Selected structural parameters of PB5Con

	MCH	MeCN	Water
	S_{GS}	S_{GS}	S_{GS}
bond lengths			
C3-C4	1.46140	1.47293	1.47271
C8=09	1.21884	1.21314	1.21338
C11-C13	1.47999	1.48025	1.48026
C16-C19	1.51028	1.50793	1.50782
bond angles			
N1-C3-C4	121.80838	122.39180	122.43560
N2=C3-C4	126.87375	125.25672	125.22417
C4-C8=O9	125.50303	125.06738	125.07327
C10=C11-C13	120.67736	120.87320	120.87941
C12-C11-C13	120.84762	120.83442	120.82343
C17-C16-C19	120.59876	120.72273	120.74369
dihedral angles			
N1-C3-C4=C5	-1.28223	-80.09705	-78.68284
2N=C3-C4-C8	-1.55253	-79.61633	-78.13192
C3-C4-C8=O9	0.64188	-1.75345	-1.72350
C10=C11-C13-C14	-38.89246	-38.38059	-38.29679
C12-C11-C13=C18	-38.68051	-38.34069	-38.21442

Table S3. Selected structural parameters of PB5-Tri(LYS)

	PB5					
	E_{HOMO}	E_{LUMO}	E_{GAP}	η	μ	χ
GP	-6.0426	-2.6833	3.3593	1.6796	-4.3629	4.3629
MCH	-5.9571	-2.7617	3.1954	1.5977	-4.3594	4.3594
1,4-Dx	-5.9612	-2.7587	3.2025	1.6013	-4.3599	4.3599
Et_2O	-5.9936	-2.7451	3.2485	1.6243	-4.3693	4.3693
EtAc	-6.0083	-2.7413	3.2670	1.6335	-4.3748	4.3748
THF	-6.0162	-2.7391	3.2771	1.6385	-4.3776	4.3776
MeAc	-6.0412	-2.7347	3.3065	1.6532	-4.3880	4.3880
MeCN	-6.2175	-2.5736	3.6439	1.8220	-4.3956	4.3956
DMF	-6.2178	-2.5736	3.6442	1.8221	-4.3957	4.3957
DMSO	-6.2203	-2.5731	3.6472	1.8236	-4.3967	4.3967
Water	-6.2175	-2.5736	3.6439	1.8220	-4.3956	4.3956

	PB5Con						PB5-Tri(LYS)					
	E_{HOMO}	E_{LUMO}	E_{GAP}	η	μ	χ	E_{HOMO}	E_{LUMO}	E_{GAP}	η	μ	χ
GP	-5.8053	-2.5976	3.2077	1.6038	-4.2014	4.2014						
MCH	-5.8817	-2.6272	3.2545	1.6273	-4.2545	4.2545	-5.8314	-2.5987	3.2327	1.6164	-4.2150	4.2150
1,4-Dx	-5.8910	-2.6305	3.2605	1.6302	-4.2607	4.2607	-5.8406	-2.6022	3.2384	1.6192	-4.2214	4.2214
Et_2O	-5.9500	-2.6531	3.2970	1.6485	-4.3016	4.3016	-5.9002	-2.6259	3.2744	1.6372	-4.2630	4.2630
EtAc	-5.9737	-2.6626	3.3111	1.6556	-4.3182	4.3182	-5.9245	-2.6354	3.2891	1.6445	-4.2799	4.2799
THF	-5.9860	-2.6672	3.3187	1.6594	-4.3266	4.3266	-5.9411	-2.6419	3.2991	1.6496	-4.2915	4.2915
MeAc	-6.1936	-2.5156	3.6780	1.8390	-4.3546	4.3546	-6.1577	-2.5007	3.6570	1.8285	-4.3292	4.3292
MeCN	-6.2058	-2.5186	3.6872	1.8436	-4.3622	4.3622	-6.1672	-2.5039	3.6633	1.8316	-4.3356	4.3356
DMF	-6.2064	-2.5189	3.6875	1.8437	-4.3627	4.3627	-6.1677	-2.5039	3.6638	1.8319	-4.3358	4.3358
DMSO	-6.2099	-2.5197	3.6902	1.8451	-4.3648	4.3648	-6.1705	-2.5050	3.6654	1.8327	-4.3378	4.3378
Water	-6.2058	-2.5186	3.6872	1.8436	-4.3622	4.3622	-6.1748	-2.5067	3.6682	1.8341	-4.3407	4.3407

Table S4. The frontier orbital energies in selected solvents for 4HGL-4'CHO. All values are given in eV

	PB5		PB5Con		PB5-Tri(LYS)	
	q_{CT}	D_{CT}	q_{CT}	D_{CT}	q_{CT}	D_{CT}
MCH	0.730	4.199	0.730	4.040	0.736	3.997
1,4-Dx	0.732	4.207	0.732	4.043	0.737	4.125
Et_2O	0.743	4.383	0.742	4.235	0.740	4.220
EtAc	0.748	4.441	0.744	4.229	0.742	4.291
THF	0.750	4.467	0.745	4.325	0.742	4.347
MeAc	1.214	4.547	1.209	4.627	1.233	4.667
MeCN	1.219	4.707	1.206	4.648	1.221	4.694
DMF	1.218	4.706	1.206	4.649	1.220	4.693
DMSO	1.216	4.712	1.205	4.652	1.217	4.689
Water	1.219	4.725	1.205	4.665	1.212	4.677

Table S5. CT parameters for the bright low-lying excited state

	B3LYP	ωB97XD	CAM-B3LYP	HSE1PBE	PBE0	mPW1PBE	mPW3PBE
GP	484.24	340.92	356.73	483.89	464.08	454.58	480.74
MCH	486.10	383.86	396.24	483.61	463.02	464.08	482.40
1,4-Dx	485.02	383.11	395.43	482.50	454.81	463.02	481.32
Et_2O	476.58	377.38	389.18	473.90	452.61	454.81	472.82
EtAc	474.30	376.03	387.64	471.56	451.88	452.61	470.52
THF	473.55	375.70	387.21	470.77	446.77	451.88	469.76
MeAc	468.20	372.37	383.53	465.33	420.50	446.77	464.39
MeCN	450.40	314.20	324.67	449.12	420.48	420.50	446.47
DMF	450.35	314.23	324.83	449.06	420.01	420.48	446.42
DMSO	449.79	314.14	324.79	448.48	418.93	420.01	445.87
Water	448.64	313.87	323.81	447.32	464.08	418.93	444.72

Table S6. The values of vertical excitation energies (in nm) of PB5

	B3LYP	ωB97XD	CAM-B3LYP	HSE1PBE	PBE0	mPW1PBE	mPW3PBE
MCH	494.67	382.45	396.82	492.65	471.03	471.50	490.70
Dx	494.20	381.82	396.17	492.14	470.48	470.92	490.19
Et2O	487.96	376.83	390.71	485.76	464.12	464.54	483.84
EtAc	487.29	375.56	389.44	485.07	463.20	463.62	483.11
THF	487.86	375.21	389.17	485.66	463.55	463.96	483.64
MeAc	483.01	372.07	385.61	480.73	458.81	459.20	478.74
MeCN	525.14	317.16	351.33	524.74	484.15	484.15	519.81
DMF	539.04	317.71	355.49	538.85	495.84	495.84	533.45
DMSO	536.13	317.54	354.26	535.87	493.39	493.39	530.58
Water	521.62	316.79	349.55	521.16	481.12	481.10	516.35

Table S7. The values of cLR excitation energies (in nm) of PB5

	PB5		PB5Con	
	μ_g	μ_{CT}	μ_g	μ_{CT}
GP	3.22	20.66	3.86	9.23
MCH	1.85	15.29	4.26	10.23
1,4-Dx	1.86	15.44	4.30	10.32
Et_2O	1.99	16.24	4.49	10.77
EtAc	2.05	16.50	4.53	10.90
THF	2.09	16.62	4.55	10.98
MeAc	2.21	16.99	9.67	22.76
MeCN	4.92	27.32	9.80	22.66
DMF	4.93	27.31	9.81	22.62
DMSO	4.98	27.30	9.85	22.59
Water	5.00	27.40	9.89	22.52

Table S8. Calculated values of dipole moments (in D) for the ground and CT excited state

	B3LYP	ωB97xD	CAM-B3LYP	HSE1PBE	PBE0	mPW1PBE	mPW3PBE
GP	560.22	427.11	446.03	557.77	533.46	534.13	555.41
MCH	563.77	437.28	454.95	560.95	537.64	538.30	558.71
1,4-Dx	562.23	437.03	454.51	559.36	536.28	536.93	557.16
Et_2O	553.79	436.48	452.81	550.53	528.93	529.49	548.65
EtAc	552.00	437.10	453.06	548.61	527.45	527.99	546.83
THF	571.63	389.30	411.37	571.10	533.34	533.49	565.70
MeAc	544.39	414.76	431.11	541.86	516.56	516.85	539.22
MeCN	542.47	415.84	431.88	539.78	515.16	515.45	537.30
DMF	544.63	417.54	433.62	541.92	517.20	517.49	539.43
DMSO	543.93	417.66	433.66	541.18	516.64	516.93	538.73
Water	540.94	414.74	430.71	538.22	513.67	513.95	535.76

Tabele S9. The values of vertical de-excitation energies (in nm) of PB5

Lysine residues	ΔG_b	*K*i	Intermolecular energy	Binding energy
30	-3.8	9.720	-3.64	-2.75
35	-5.5	0.487	-5.73	-4.83
36	-4.8	2.530	-4.44	-3.54
39	-4.4	2.550	-4.43	-3.54
46	-5.5	0.486	-5.42	-4.52
59	-5.1	2.620	-4.42	-3.52
101	-5.8	0.368	-5.58	-4.68
114	-5.5	0.565	-5.33	-4.43
116	-6.2	0.317	-5.67	-4.77
135	-4.2	7.300	-3.81	-2.92
138	-5.0	0.896	-5.05	-4.16
200	-4.1	1.490	-4.75	-3.86
Ter	-3.4	19.39	-3.23	-3.23

Table S10. Binding free energies (ΔG_b, kcal/mol) obtained during AutoDock simulations. Ki is given in [mM]