Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Synthon Crossover between Halogen…π and Halogen…Halogen Interaction

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Experimental section.

Chemicals and instrumentation: All solvents such as methanol and pyridine and the chemicals, 2-naphthoic acid, quinaldic acid, as well as 4-Flouro, Chloro, Bromo and Iodo aniline were commercially available (reagent grade) and were purchased from Merck and used without further purification. Infrared spectra (4000–400 cm-1) of solid samples were taken as 1% dispersion in KBr pellets using a BOMEM - MB102 spectrometer. ^{1}H NMR spectra were recorded on a Bruker AC-300 MHz spectrometer at ambient temperature in CD_3OD. All chemical shifts are quoted in part per million (ppm) relative to tetramethylsilane. Melting point was obtained by a Bamstead Electrothermal type 9200 melting point apparatus and corrected.

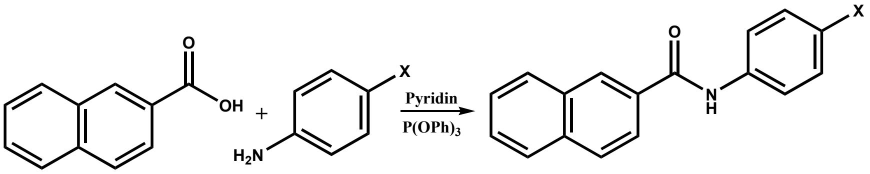
Synthesis of N-(4-fluorophenyl)-2-naphthamide, naph-F: A solution of 5mmol 4-Chloroaniline in 15 mL pyridine was added to a solution of 5mmol 2-naphthoic acid in 15 mL pyridine, equation 1. The resulting solution was stirred at 313 K for 20 min, then 5mmol triphenyl phosphite (1.3 mL) was added dropwise, and the reaction mixture was stirred 5 h at 373 K for 24 h at ambient temperature. The resulting solution was added to distilled water. A white solid resulted with a yield of 84%. X-ray quality crystals were obtained by slow evaporation of the methanolic solution of this compound for seven days. Anal. Calcd for naph-F: C, 76.97; H, 4.56; N, 5.28. Found: C, 76.89; H, 4.53; N, 5.25. ^{1}H NMR (CD3OD, δ ppm): 10.58(1H), 8.58(1H), 8.40(1H), 7.83(1H), 7.62-7.68(4H), 7.43-7.65(4H). Selected IR (KBr pellet, cm^{-1}): 3377, 1653, 1600, 1520, 1410, 1308, 1241, and 1102. (Melting point: 481-483K).

Synthesis of N-(4-chlorophenyl)-2-naphthamide, naph-Cl: A solution of 5mmol 4-Chloroaniline in 15 mL pyridine was added to a solution of 5mmol 2-naphthoic acid in 15 mL pyridine, equation 1. The resulting solution was stirred at 313 K for 20 min, then 5mmol triphenyl phosphite (1.3 mL) was added dropwise, and the reaction mixture was stirred 5 h at 373 K for 24 h at ambient temperature. The resulting solution was added to distilled water. A white solid resulted with a yield of 92%. X-ray quality crystals were obtained by slow evaporation of the methanolic solution of this compound for five days. Anal. Calcd for naph-Cl: C, 72.47; H, 4.27; N, 4.97. Found: C, 72.41; H, 4.2; N, 4.83. ^{1}H NMR (CD3OD, δ ppm): 10.58(1H), 8.58(1H), 8.40(1H), 7.83(1H), 7.62-7.68(4H), 7.43-7.65(4H). Selected IR (KBr pellet, cm^{-1}): 3377, 1650, 1605, 1520, 1420, 1308, 1241, and 1100. (Melting point: 490-492K).

Synthesis of N-(4-bromophenyl)-2-naphthamide, naph-Br: A solution of 5mmol 4-Bromoaniline in 15 mL pyridine was added to a solution of 5mmol 2-naphthoic acid in 15 mL pyridine, equation 1. The resulting solution was stirred at 313 K for 20 min, then 5mmol triphenyl phosphite (1.3 mL) was added dropwise, and the reaction mixture was stirred 5 h at 373 K for 24 h at ambient temperature. The resulting solution was added to distilled water. A white solid resulted with a yield of 89%. X-ray quality crystals were obtained by slow evaporation of the methanolic solution of this compound for two days. Anal. Calcd for naph-Br: C, 62.6; H, 3.71; N, 4.97. Found, C, 62.56; H, 3.65; N, 4.85. ^{1}H NMR (CD3OD, δ ppm): 10.58(1H), 8.58(1H), 8.40(1H), 7.83(1H), 7.62-7.68(4H), 7.43-7.65(4H). Selected IR (KBr pellet, cm^{-1}): 3377, 1653, 1600, 1520, 1410, 1308, 1241, and 1102. (Melting point: 485-487K).

Synthesis of N-(4-iodophenyl)-2-naphthamide, naph-I: A solution of 5mmol 4-Iodoaniline in 15 mL pyridine was added to a solution of 5mmol 2-naphthoic acid in 15 mL pyridine, equation 1. The resulting solution was stirred at 313 K for 20 min, then 5mmol triphenyl phosphite (1.3 mL) was added dropwise, and the reaction mixture was stirred 5 h at 373 K for 24 h at ambient temperature. The resulting solution was added to distilled water. A white solid resulted with a yield of 85%. X-ray quality crystals were obtained by slow evaporation of the methanolic solution of this compound for three days. Anal. Calcd for naph-I: C, 54.71; H, 3.24; N, 3.75.

Found: C, 54.6; H, 3.15; N, 3.62. ^{1}H NMR (CD3OD, δ ppm): 10.58(1H), 8.6(1H), 8.11(1H), 7.87(1H),7.62-7.68(4H),7.43-7.65(4H). Selected IR (KBr pellet, cm^{-1}): 3377, 1659, 1600, 1520, 1487, 1394, 1235, 1102. (Melting point: 491-493K).



X = I, Br, Cl, and F

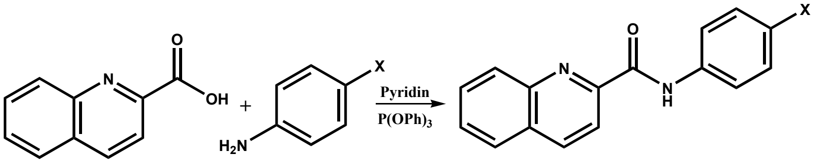
Equation 1.

Synthesis of N-(4-fluorophenyl) quinoline-2-carboxamide, quin-F: A solution of 5mmol 4-fluoroaniline in 15 mL pyridine was added to a solution of 5mmol quinaldic acid in 15 mL pyridine, equation 2. The resulting solution was stirred at 353 K for 20 min, then 5mmol triphenyl phosphite (1.3 mL) was added dropwise, and the reaction mixture was stirred 5 h at 363 K for 24 h at ambient temperature. The resulting solution was added to distilled water. A pale yellow solid resulted with a yield of 85%. X-ray quality crystals were obtained by slow evaporation of the methanolic solution of these compounds.). Anal. Calcd for quin-F: C, 72.17; H, 4.16; N, 10.52. Found, C, 72,14; H, 4.14; N, 10.49. ^{1}H NMR (CD3OD, δ ppm): 10.85(1H), 8.60(1H), 8.33(1H), 8.04(1H), 7.80-7.93(4H), 7.55-7.70(3H). Selected IR (KBr pellet, cm-1): 3363, 1700, 1593, 1520, 1387, 1308, 1202, and 1069. (Melting point: 395-397 K).

Synthesis of N-(4-chlorophenyl) quinoline-2-carboxamide, quin-Cl: A solution of 5mmol 4-Cloroaniline in 15 mL pyridine was added to a solution of 5mmol quinaldic acid in 15 mL pyridine, equation 2. The resulting solution was stirred at 313 K for 20 min, then 5mmol triphenyl phosphite (1.3 mL) was added dropwise, and the reaction mixture was stirred 5 h at 373 K for 24 h at ambient temperature. The resulting solution was added to distilled water. A pale yellow solid resulted with a yield of 88%. X-ray quality crystals were obtained by slow evaporation of the methanolic solution of these compounds. Anal. Calcd for quin-Cl: C, 67.97; H, 3.92; N, 9.91. Found, C, 67.94; H, 3.89; N, 9.86. ^{1}H NMR (CD3OD, δ ppm): 10.85(1H), 8.60(1H), 8.33(1H), 8.04(1H), 7.80-7.93(4H), 7.55-7.70(3H). Selected IR (KBr pellet, cm^{-1}): 3360, 1695, 1590, 1520, 1387, 1202, 1122, and 1069. (Melting point: 400-402 K).

Synthesis of N-(4-bromorophenyl) quinoline-2-carboxamide, quin-Br: A solution of 5mmol 4-Bromoaniline in 15 mL pyridine was added to a solution of 5mmol quinaldic acid in 15 mL pyridine, equation 2. The resulting solution was stirred at 313 K for 20 min, then 5mmol triphenyl phosphite (1.3 mL) was added dropwise, and the reaction mixture was stirred 5 h at 373 K for 24 h at ambient temperature. The resulting solution was added to distilled water. A pale yellow solid resulted with a yield of 85%. X-ray quality crystals were obtained by slow evaporation of the methanolic solution of these compounds. Anal. Calcd for quin-4Br: C, 58.74; H, 3.39; N, 8.56. Found, C, 58.72; H, 3.34; N, 8. 52. ^{1}H NMR (CD3OD, δ ppm): 10.85(1H), 8.60(1H), 8.33(1H), 8.04(1H), 7.80-7.93(4H), 7.55-7.70(3H), Selected IR (KBr pellet, cm^{-1}): 3357, 1690, 1585, 1520, 1390, 1308, 1241, and 1005. (Melting point: 431-433 K).

Synthesis of N-(4-iodophenyl) quinoline-2-carboxamide, quin-I: A solution of 5mmol 4-Iodoaniline in 15 mL pyridine was added to a solution of 5mmol quinaldic acid in 15 mL pyridine, equation 2. The resulting solution was stirred at 313 K for 20 min, then 5mmol triphenyl phosphite (1.3 mL) was added dropwise, and the reaction mixture was stirred 5 h at 373 K for 24 h at ambient temperature. The resulting solution was added to distilled water. A pale yellow solid resulted with a yield of 81%. X-ray quality crystals were obtained by slow evaporation of the methanolic solution of these compounds. Anal. Calcd for quin-I: C, 51.36; H, 2.96; N, 7.49. Found: C, 51.35; H , 2.94; N, 7.46. ^{1}H NMR (CD3OD, δ ppm): 10.85(1H), 8.60(1H), 8.30(1H), 8.05(1H), 7.80-7.92(4H), 7.57-7.72(3H), Selected IR (KBr pellet, cm^{-1}): 3357, 1693, 1580, 1520, 1394, 1308, 1129, and 1003. (Melting point: 440-442K).



X = I, Br, Cl, and F

Equation2.

Single crystal data collection and refinement.

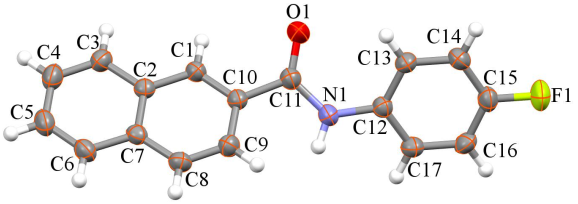
The X-ray diffraction measurements were made on a STOE IPDS-II or STOE-IPDS-2T diffractometers with graphite monochromated Mo-Kα radiation. For all compound suitable single crystals were mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data. Data were collected at a temperature of 298(2) K in an a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [S1] software package. A numerical absorption correction was applied using X-RED [S2] and X-SHAPE [S3] software's. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods [S4]. All of hydrogen atoms were located in an ideal position and then refined isotropically. Atomic factor are from International Tables for X-ray Crystallography [S5]. All refinements were performed using the X-STEP32 crystallographic software package [S6]. ORTEP diagrams of these complexes are shown in figure S1. Crystallographic details including crystal data and structure refinement are listed in Table S1.

Computational details for calculating halogen bonding binding energies.

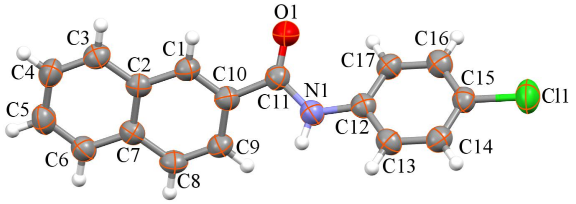
DFT calculations were performed using the ORCA quantum chemistry suite.[S7] The local spin density approximation (LSD) exchange correlation potential was used with the local density approximation of the correlation energy.[S8] Gradient-corrected geometry optimizations [S9] were performed by using the generalized gradient approximation (Perdew–Wang non-local exchange and correlation corrections – PW91).[S10] The selected two fragments were cut out directly from the CIF data without optimization. Large atom basis sets TZP are used to ascribe all the atoms here. A frozen core approximation was used to treat the core electrons: (1s) for C and N, (4p) for I, (3p) for Br, (2p) for Cl, (1s) for O and F. Scalar relativistic effects were taken into account by using the zeroth-order regular approximation (ZORA).[S11]

Computational details for generating molecular electrostatic potential surface.

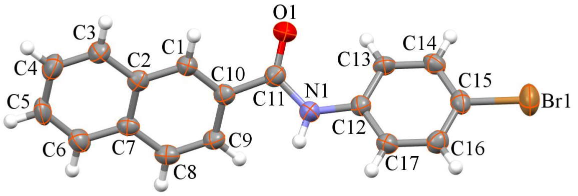
Electrostatic potential surfaces were generated for **naph-F**, **quin-F**, **naph-Cl**, **quin-Cl**, **naph-Br**, **quin-Br**, **naph-I** and **quin-I** from DFT calculations performed at the B3LYP/6-311G (d,p) basis set for all atoms except iodine, and the LANL2DZdp-ECP (with polarization functions of *d* symmetry and diffuse functions of *p* symmetry) basis set for iodine. Potential surfaces were mapped by conventional molecular electron density (0.02 electron/ Bohr^3) and color-coding.



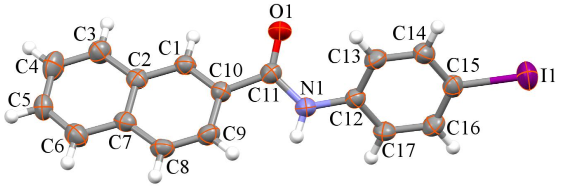
(a) naph-F



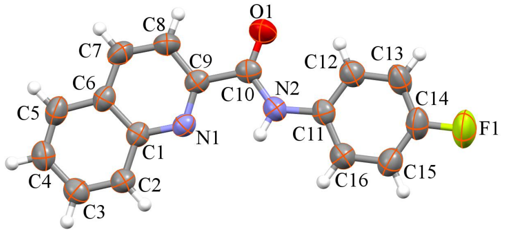
(b) naph-Cl



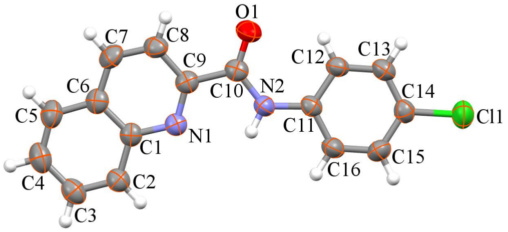
(c) naph-Br



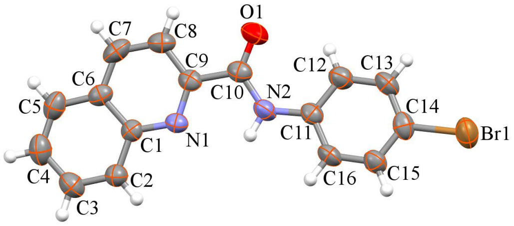
(d) naph-I



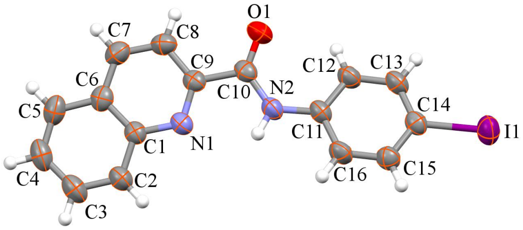
(e) quin-F



(f) quin-Cl



(g) quin-Br



(h) quin-I

Figure S1: *ORTEP* diagrams of compounds **naph-X**, a-d, and **quin-X**, e-h, drawn with 30% ellipsoid probability.

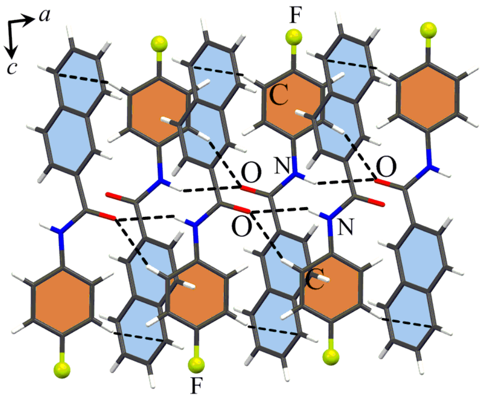


Figure S2. A side view representation of **naph-F**, showing the generation of 2D sheets, in *ac*-plane, through the N-H…O=C and C_{phen}-H…O hydrogen bonds. These 2D sheets are further linked to each other via C-H…π interactions in *b*-direction.

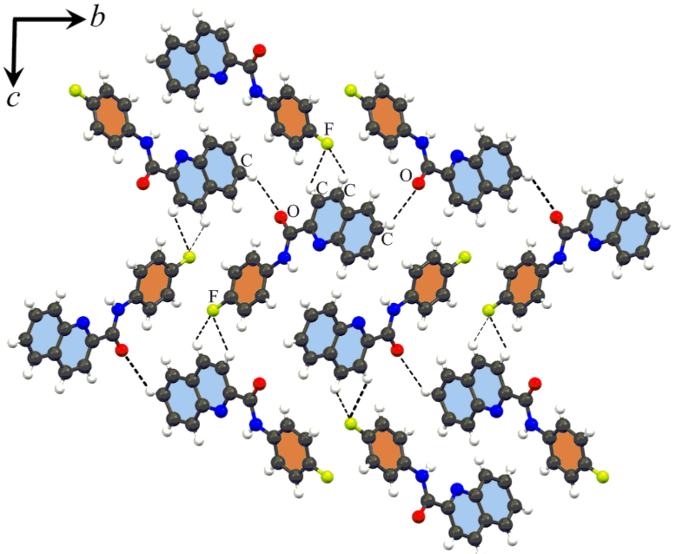


Figure S3. A side view representation of **quin-F**, showing the generation of 2D sheets, in *bc*-plane, through the N-H…O=C and C-H…F hydrogen bonds.

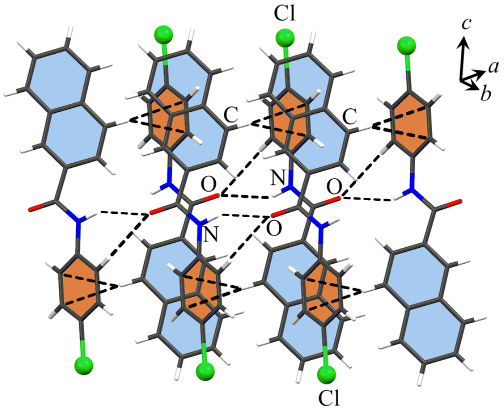


Figure S4. A side view representation of **naph-Cl**, showing the generation of 2D sheets, in *ac*-plane, through the N-H…O=C and C_{phen}-H…O hydrogen bonds. These 2D sheets are further linked to each other via C-H…π interactions.

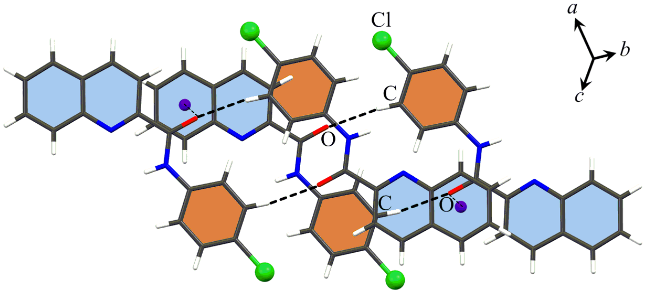


Figure S5. A side view representation of **quin-Cl**, showing the association of the adjacent molecules through C=O…H-C$_{phen}$ hydrogen bonds that are cooperated with C=O…π interactions, in *b*-direction, to form a 3D crystal packing.

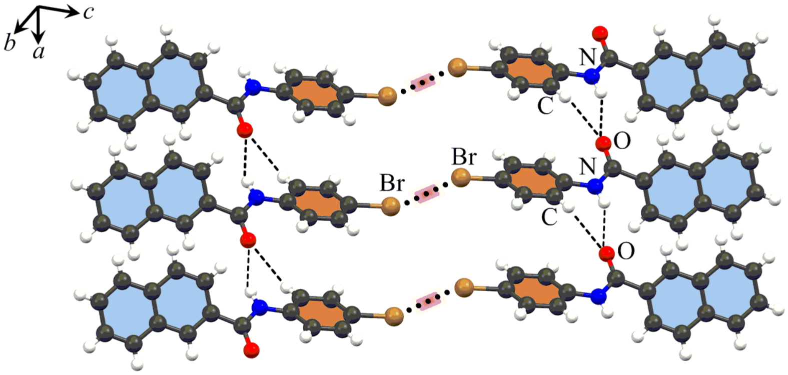


Figure S6. A side view representation of **naph-Br**, showing the association of the adjacent molecules through N-H…O and C$_{phen}$-H…O hydrogen bonds that are cooperated with Br…Br interactions, in *c*-direction, to form a 3D crystal packing. X…X interactions are highlighted in red.

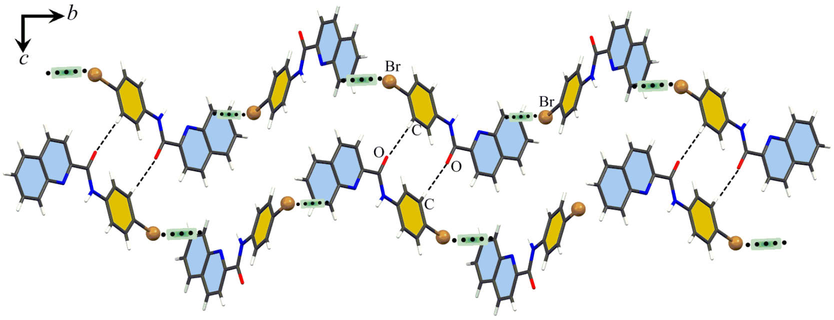


Figure S7. A side view representation of **quin-Br**, showing how dimeric units are formed by C=O…H-C$_{phen}$ hydrogen bonds. Adjacent dimeric units are further linked to each other by C-Br…π halogen bonds to generate a wave-like chain. Halogen… π interactions are highlighted in green.

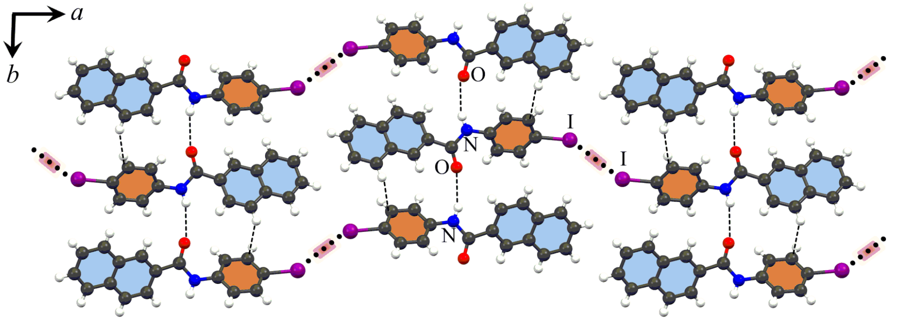


Figure S8. A side view representation of **naph-I**, showing the association of the adjacent molecules through N-H…O hydrogen bonds and C_{phen}-H… π interactions that are cooperated with I…I interactions, in *a*-direction, to form a 3D crystal packing. X…X interactions are highlighted in red.

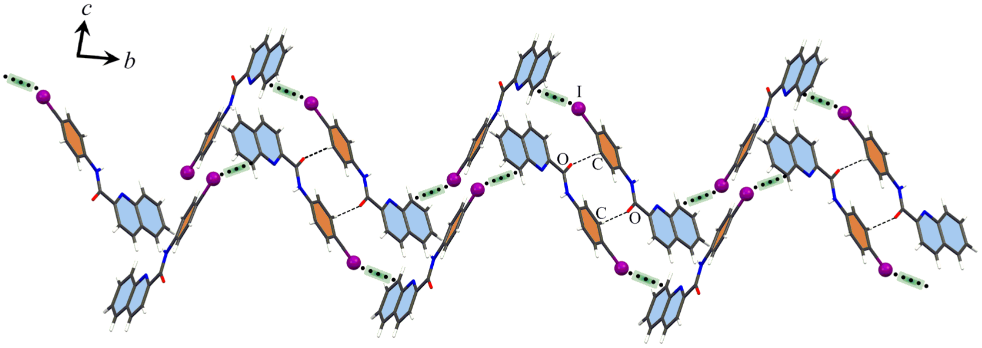


Figure S9. A side view representation of **quin-I**, showing how dimeric units are formed by C=O…H-C_{phen} hydrogen bonds. Adjacent dimeric units are further linked to each other by C-I…π halogen bonds to generate a wave-like chain. Halogen… π interactions are highlighted in green.

Table S1. Structural data and refinement for compounds **naph-X** and **quin-X**.

	naph-F	**naph-Cl**	**naph-Br**	**naph-I**
formula	$C_{17}H_{12}FNO$	$C_{17}H_{12}ClNO$	$C_{17}H_{12}BrNO$	$C_{17}H_{12}INO$
fw	265.28	281.73	326.18	373.18
λ/Å	0.71073	0.71073	0.71073	0.71073
T/K	298(2)	298(2)	298(2)	298(2)
crystal.system	Triclinic	Triclinic	Triclinic	Monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	5.6099(14)	5.5931(12)	5.5791(16)	32.1685(16)
b/Å	7.6163(19)	7.6167(19)	7.683(3)	10.7211(4)
c/Å	14.943(3)	15.880(4)	16.223(4)	8.2676(5)
α/°	88.730(19)	88.41(2)	89.07(2)	90.0
β/°	84.005(19)	83.971(18)	83.89(2)	95.678(4)
γ/°	85.28(2)	84.915(19)	84.51(3)	90.0
V/Å^3	632.8(3)	670.0(3)	688.3(4)	2837.4(2)
D_{calc}/Mg m^{-3}	1.392	1.396	1.574	1.747
Z	2	2	2	8
μ/mm^{-1}	0.097	0.279	2.980	2.251
F(000)	276	292	328	1456
2θ/°	58.3	58.5	58.3	58.3
R(int)	0.0974	0.0951	0.1031	0.0524
GOOF	1.076	1.166	1.179	1.110
$R_1{}^a(I > 2\sigma(I))$	0.0631	0.0954	0.0754	0.0536
$wR_2{}^b(I > 2\sigma(I))$	0.1718	0.1231	0.1368	0.1177
CCDC No.	947153	947152	947151	947154
	quin-F[c]	**quin-Cl**	**quin-Br**	**quin-I**
formula	$C_{16}H_{11}FN_2O$	$C_{16}H_{11}ClN_2O$	$C_{16}H_{11}BrN_2O$	$C_{16}H_{11}IN_2O$
fw	266.27	282.72	327.17	374.17
λ/Å	0.71073	0.71073	0.71073	0.71073
T/K	298(2)	298(2)	298(2)	298(2)
crystal.system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	4.9506(3)	14.176(3)	6.364(3)	6.548(2)
b/Å	14.5932(14)	6.0252(11)	17.187(9)	17.029(5)
c/Å	17.6779(13)	15.551(4)	12.649(7)	12.714(5)
β/°	90.0	98.311(19)	102.71(4)	102.06(3)
V/Å^3	1277.14(17)	1314.3(5)	1349.5(12)	1386.5(8)
D_{calc}/Mg m^{-3}	1.385	1.429	1.610	1.793
Z	4	4	4	4
μ/mm^{-1}	0.098	0.286	3.042	2.306
F(000)	552	584	656	728
2θ/°	58.4	59.3	59.3	58.4
R(int)	0.0912	0.0901	0.0951	0.0859
GOOF	1.093	1.160	1.150	1.157
$R_1{}^a(I > 2\sigma(I))$	0.0731	0.0826	0.0843	0.0411
$wR_2{}^b(I > 2\sigma(I))$	0.1387	0.1223	0.1432	0.1154
CCDC No.	947157	947156	947155	948750

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)2]^{1/2}$. ^{c} Flack parameter = -0.01(17)

Table S2. Selected hydrogen bond geometries for compounds **naph-X** and **quin-X**.

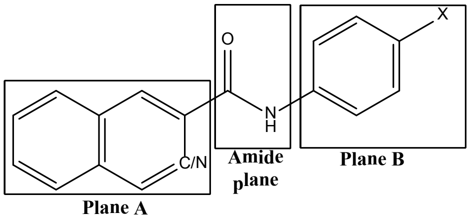
Structure	D-H…A	d(D-H) (Å)	d(H…A) (Å)	d(D…A) (Å)	<D-H…A/°	Symmetry
naph-F	N1-H1B…O1	0.860	2.600(2)	3.399(3)	155.1(1)	1+x,y,z
	C17-H17…O1	0.930	2.717(2)	3.417(3)	132.7(1)	1+x,y,z
	C4-H4…F1	0.930	2.703(2)	3.273(3)	120.4(2)	1+x, y, -1+z
naph-Cl	N1-H1B...O1	0.860	2.587(3)	3.386(5)	155.1(2)	-1+x,y,z
	C13-H13...O1	0.930	2.702(4)	3.406(6)	133.1(3)	-1+x,y,z
naph-Br	N1-H1B…O1	0.860	2.572(3)	3.373(5)	155.2(3)	-1+x,y,z
	C17-H17…O1	0.930	2.695(4)	3.394(6)	132.7(3)	-1+x,y,z
naph-I	N1-H1B…O1	0.860	2.372(3)	3.184(5)	157.5(2)	½-x,-1/2+y,-1/2+z
	C9-H9…O1	0.930	2.815(3)	3.600(5)	142.9(3)	½-x,-1/2+y,-1/2+z
quin-F	C4-H4…O1	0.930	2.679(2)	3.366(4)	131.3(2)	-x,1/2+y,1.5-z
	C8-H8…F1	0.930	2.593(2)	3.234(4)	126.4(2)	1.5-x,-y,-1.2+z
quin-Cl	C13-H13...O1	0.930	2.371(2)	3.262(4)	160.2(2)	2-x,-y,1-z
quin-Br	C13-H13...O1	0.930	2.381(4)	3.229(7)	151.5(3)	2-x,-y,1-z
quin-I	C13-H13…O1	0.930	2.406(3)	3.267(5)	154.0(2)	-x, -y, 1-z

Table S3. π-π, C=O…π and C-H…π interaction geometries for compounds **naph-X** and **quin-X**.

Structure	Interaction	Type of interaction	H/centroid-centroid distance(Å)
naph-F	C-H…π	C_{naph}-H…π_{phen}	2.707, 2.712
naph-Cl	C-H…π	C_{naph}-H…π_{phen}	2.698, 2.720
naph-Br	C-H…π	C_{naph}-H…π_{phen}	2.742, 2.757
naph-I	C-H…π	C_{naph}-H…π_{naph}	2.828
quin-F	π-π Stacking[a]	π_{quin}-π_{quin}	3.673
	C=O…π	CO…π_{quin}	3.762
quin-Cl	C=O…π	CO…π_{quin}	3.564
quin-Br	C=O…π	CO…π_{quin}	3.693
quin-I	C=O…π	CO…π_{quin}	3.679

[a] The angles between quinolone rings and the displacement angle (the angle between the C-C direction and quinoline ring normal vector) are 1.4° and 18.3°, respectively.

Table S4. Dihedral angles between plane A, plane B and amide plane (plane A = naphthalene or quinoline ring, plane B = phenyl ring).

Structure	∠ amide plane and plane A (/°)	∠ amide plane and plane B (/°)	∠ plane A and plane B (/°)	Definition of geometrical parameters
naph-F	29.09	27.63	55.93	
naph-Cl	29.37	27.01	55.61	
naph-Br	29.91	27.12	55.92	
naph-I	25.63	38.48	63.96	
quin-F	3.59	6.32	3.92	
quin-Cl	5.07	7.02	10.34	
quin-Br	3.08	12.36	13.35	
quin-I	3.85	10.78	12.79	

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