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Supplementary material

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Table S1

BSSE corrected interaction energies ($E_{\mathrm{int}}^{\mathrm{cor}}$) for the adsorption complexes formed between 44BPY and 32T, and contributions of pyridyl PY and pyridinium PYH^+ rings (E_{cont}) to $E_{\mathrm{int}}^{\mathrm{cor}}$ with estimated steric (E_{ster}) and dispersion energies (E_{disp}) at the M062X/6-31++G(2d,2p) level[a]

Species		PY_{op}			PY_{cl}			$(PYH^+)_{op}$			$(PYH^+)_{cl}$		
	$E_{\mathrm{int}}^{\mathrm{cor}}$	E_{cont}	E_{ster}	E_{disp}	E_{cont}	E_{ster}	E_{disp}	E_{cont}	E_{ster}	E_{disp}	E_{cont}	E_{ster}	E_{disp}
44BPY / 32T	-43.5	-26.7	0.0	-17.0	-16.4	+17.6	-24.3						
$(44BPYH^+ / 32T^-)_{op}$	-117.1				-19.9	+17.0	-24.2	-101.6	0.0	-18.4			
$(44BPYH^+ / 32T^-)_{cl}$	-121.6	-29.8	0.0	-17.1							-97.7	+11.1	-25.7
$44BPYH_2^{2+} / 32T^{2-}$	-290.8							-139.0	0.0	-18.9	-136.5	+9.5	-25.9

[a] Energies are given in kcal/mol.

Table S2

BSSE corrected interaction energies ($E_{\mathrm{int}}^{\mathrm{cor}}$) for the adsorption complexes formed between 44BPY and 32T, and contributions of pyridyl PY and pyridinium PYH^+ rings (E_{cont}) to $E_{\mathrm{int}}^{\mathrm{cor}}$ with estimated steric (E_{ster}) and dispersion energies (E_{disp}) at the M062X-D3/6-31++G(2d,2p) level[a]

Species	$E_{\mathrm{int}}^{\mathrm{cor}}$	PY_{op}			PY_{cl}			$(PYH^+)_{op}$			$(PYH^+)_{cl}$		
		E_{cont}	E_{ster}	E_{disp}	E_{cont}	E_{ster}	E_{disp}	E_{cont}	E_{ster}	E_{disp}	E_{cont}	E_{ster}	E_{disp}
44BPY / 32T	-49.6	-30.0	0.0	-20.3	-19.7	+17.6	-27.7						
$(44BPYH^+ / 32T^-)_{op}$	-123.4				-23.3	+17.0	-27.6	-105.1	0.0	-21.9			
$(44BPYH^+ / 32T^-)_{cl}$	-128.0	-33.1	0.0	-20.4							-101.3	+11.1	-29.4
$44BPYH_2^{2+} / 32T^{2-}$	-297.2							-142.5	0.0	-22.4	-140.0	+9.5	-29.4

[a] Energies are given in kcal/mol.

Table S3

BSSE corrected interaction energies ($E_{\mathrm{int}}^{\mathrm{cor}}$) for the adsorption complexes formed between 44BPY and 32T, and contributions of pyridyl PY and pyridinium PYH^+ rings (E_{cont}) to $E_{\mathrm{int}}^{\mathrm{cor}}$ with estimated steric (E_{ster}) and dispersion energies (E_{disp}) at the B3LYP-D3/6-31++G(2d,2p) level[a]

Species	$E_{\mathrm{int}}^{\mathrm{cor}}$	PY_{op}			PY_{cl}			$(PYH^+)_{op}$			$(PYH^+)_{cl}$		
		E_{cont}	E_{ster}	E_{disp}	E_{cont}	E_{ster}	E_{disp}	E_{cont}	E_{ster}	E_{disp}	E_{cont}	E_{ster}	E_{disp}
44BPY / 32T	-55.7	-34.7	0.0	-25.0	-22.8	+17.6	-30.7						
$(44BPYH^+ / 32T^-)_{op}$	-127.9				-26.4	+17.0	-30.7	-108.6	0.0	-25.5			
$(44BPYH^+ / 32T^-)_{cl}$	-132.7	-37.7	0.0	- 25.1							-103.6	+11.1	-31.6
$44BPYH_2^{2+} / 32T^{2-}$	-301.2							-145.8	0.0	-25.7	-142.2	+9.5	-31.6

[a] Energies are given in kcal/mol.

Table S4

Experimental and calculated frequencies (cm^{-1}) of in-plane modes in the 600-1700 cm^{-1} region of free 44BPY, $44BPYH_2^{2+}$ free and complexed to H-ZSM-5

approximate description[a,b,c]		44BPY			$44BPYH_2^{2+}$			$44BPYH_2^{2+}$ / $32T^-$		
		exp[d]	B3LYP[e]	M06-2X[f]	exp[g,h]	B3LYP[e,h]	M06-2X[f,h]	exp[h] Si/Al = 13.5	B3LYP[e,h]	M06-2X[f,h]
δ_r	**(6b-B_3)**	659	663	655	638 (-21)	639 (-24)	631 (-24)	645 (-14)	642 (-21)	636 (-19)
δ_r	**(6b-B_2)**	673[h]	675	667		651 (-24)	642 (-25)		657 (-18)	653 (-13)
δ_r, ν_{CC}, ν_{ir}	**(1-A)**	762	750	747	757 (-5)	760 (+10)	759 (+12)	760 (-2)	752 (+2)	750 (+4)
ν_{CN}, δ_r, ν_{CC}	**(12-B_1)**	989[h]	988	987	992 (+3)	1003 (+14)	1003 (+16)		1015 (+27)	1018 (+31)
δ_r, ν_{CN}, γ_{CH}	**(12-A)**	1001	994	995	1011 (+10)	10010 (+16)	1008 (+13)	1013 (+12)	1026 (+32)	1030 (+35)
δ_r, ν_{CC}	**(1-B_1)**	1038[h]	1036	1036	1031 (-7)	1039 (+3)	1036 (+1)		1039 (+3)	1037 (+1)
β_{CH} ,ν_{CN}, ν_{CC}	**(18a-B_1)**	1075[h]	1076	1073	1060 (-15)	1067 (-9)	1070 (-3)	1067 (-8)	1074 (-2)	1069 (-4)
ν_{CN}, δ_r, β_{CH}, ν_{CC}	**(18a-A)**	1075	1079	1077	1079 (+4)	1065 (-14)	1068 (-9)	1076 (+1)	1079 (0)	1083 (+6)
β_{CH}, ν_{CN}	**(9a-A)**	1216	1231	1222	1220 (+4)	1225 (-6)	1215 (-7)	1223 (+7)	1232 (+1)	1216 (-6)
β_{CH}, ν_{CN}, ν_{CC}	**(9a-B_1)**	1218[h]	1228	1220		1221 (-7)	1211 (-9)		1206 (-22)	1192 (-28)
ν_{ir}, δ_r, ν_{CC}, β_{CH}	**(Ω-A)**	1300	1291	1295	1293 (-7)	1284 (-7)	1291 (-4)	1293 (-7)	1272 (-18)	1277 (-18)
β_{CH}, ν_{CN}, ν_{CC}	**(19a-B_1)**	1487[h]	1496	1493	1502 (+15)	1509 (+12)	1504 (+11)		1510 (+13)	1503 (+10)
β_{CH}, ν_{CN}, ν_{CC}	**(19a-A)**	1514	1516	1523	1525 (+11)	1529 (+12)	1534 (+11)	1528 (+14)	1535 (+19)	1536 (+13)
ν_{CC}, β_{CH}, δ_r, ν_{CN}	**(8a-B_1)**	1589[h]	1608	1627	1630 (+41)	1652 (+44)	1669 (+42)		1650 (+41)	1652 (+36)
ν_{CC}, β_{CH}, δ_r, ν_{ir}	**(8a-A)**	1604	1614	1640	1646 (+42)	1660 (+46)	1682 (+43)	1649 (+45)	1655 (+41)	1675 (+35)

[a] ν, stretching; β, in-plane bending; γ, out-of-plane bending; δ, in-plane deformation; r, ring; ir, inter-ring. [b] Assignments with Wilson notation and symmetry in parentheses. [c] D_2 symmetry. [d] Frequencies correspond to solid 44BPY. [e] Scaling factor of ca 0.978. [f] Scaling factor of ca 0.968. [g] Raman frequencies in solid dichloride salt in ref 60.[h] Frequency shifts with respect to 44BPY in parentheses. [i] Raman frequencies in solid dibromide salt in ref 61.

Table S5

Experimental and calculated frequencies (cm^{-1}) of the in-plane Modes in the 600-1700 cm^{-1} region of free 44BPY, $44BPH^+$ free and complexed to H-ZSM-5

approximate description[a,b,c]		44BPY			$44BPYH^+$		$44BPYH^+ / 32T^-$				
								closed		open	
		exp[d]	B3LYP[e]	M06-2X[f]	B3LYP[e,g]	M06-2X[f,g]	exp[g] Si/Al = 100	B3LYP[e,g]	M06-2X[f,g]	B3LYP[e,g]	M06-2X[f,g]
δ_r	**(6b-B_3)**	659	663	655	643 (-20)	635 (-21)	652 (-7)	647 (-16)	640 (-15)	645 (-18)	640 (-15)
δ_r	**(6b-B_2)**	673[h]	675	667	669 (-6)	662 (-5)		668 (-7)	662 (-4)	673 (-2)	668 (+1)
δ_r, ν_{CC}, ν_{ir}	**(1-A)**	762	750	747	756 (+6)	755 (+8)	764 (+2)	754 (+4)	758 (+11)	751 (+1)	753 (+6)
ν_{CN}, δ_r, ν_{CC}	**(12-B_1)**	989[h]	988	987	994 (+5)	993 (+7)	994 (+5)	1004 (+15)	1010 (+23)	1006 (+18)	1006 (+19)
δ_r, ν_{CN}, γ_{CH}	**(12-A)**	1001	994	995	1004 (+10)	1003 (+7)	1012 (+11)	1017 (+22)	1017 (+22)	1021 (+27)	1025 (+29)
δ_r, ν_{CC}	**(1-B_1)**	1038[h]	1036	1036	1038 (+2)	1038 (+3)		1036 (0)	1035 (0)	1040 (+4)	1038 (+3)
β_{CH} ,ν_{CN}, ν_{CC}	**(18a-B_1)**	1075[h]	1076	1073	1060 (-15)	1065 (-8)	1064 (-11)	1075 (-1)	1071 (-2)	1073 (-3)	1072 (-1)
ν_{CN}, β_{CH}, ν_{CC}, δ_r	**(18a-A)**	1075	1079	1077	1083 (+4)	1084 (+7)	1081 (+6)	1084 (+5)	1087 (+9)	1090 (+11)	1083 (+6)
β_{CH}, ν_{CN}	**(9a-A)**	1216	1231	1222	1239 (+8)	1232 (+10)	1222 (+6)	1242 (+11)	1228 (+5)	1240 (+9)	1227 (+5)
β_{CH}, ν_{CN}, ν_{CC}	**(9a-B_1)**	1218[h]	1228	1220	1218 (-10)	1207 (-13)	1209 (-9)	1208 (-20)	1192 (-28)	1224 (-4)	1210 (-10)
ν_{ir}, δ_r, ν_{CC}, β_{CH}	**(Ω-A)**	1300	1291	1295	1300 (+9)	1304 (+10)	1290 (-10)	1279 (-12)	1278 (-17)	1278 (-13)	1284 (-10)
β_{CH}, ν_{CN}, ν_{CC}	**(19a-B_1)**	1487[h]	1496	1493	1501 (+5)	1499 (+6)	1516 (+29)	1502 (+6)	1492 (-1)	1505 (+9)	1496 (+3)
β_{CH}, ν_{CN}, ν_{CC}	**(19a-A)**	1514	1516	1523	1525 (+9)	1530 (+8)	1531 (+17)	1534 (+18)	1534 (+11)	1533 (+16)	1537 (+14)
ν_{CC}, β_{CH}, δ_r, ν_{CN}	**(8a-B_1)**	1589[h]	1608	1627	1652 (+44)	1670 (+42)	1634 (+45)	1653 (+45)	1665 (+38)	1651 (+43)	1672 (+44)
ν_{CC}, β_{CH}, δ_r, ν_{ir}	**(8a-A)**	1604	1614	1640	1604 (-10)	1630 (-10)	1615 (+11)	1620 (+5)	1645 (+5)	1620 (+6)	1640 (0)

[a] ν, stretching; β, in-plane bending; γ, out-of-plane bending; δ, in-plane deformation; r, ring; ir, inter-ring. [b] Assignments with Wilson notation and symmetry are given for 44BPY in parentheses. [c] D_2 symmetry. [d] Frequencies correspond to solid 44BPY. [e] Scaling factor of ca 0.978. [f] Scaling factor of ca 0.968. [g] Frequency shifts with respect to 44BPY in parentheses. [h] IR frequencies in ref 54.